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THE PHYSICS OF CRYSTALS

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THE PHYSICS OF CRYSTALS

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FIRST EDITION



McGRAW-HILL BOOK COMPANY, INC.

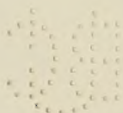
NEW YORK: 370 SEVENTH AVENUE

LONDON: 6 & 8 BOUVERIE ST., E. C. 4

1928

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PRINTED IN THE UNITED STATES OF AMERICA



THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

The University of California, in inviting me to give a course of lectures for a semester, has given me the opportunity to organize into a consistent system the results of a number of investigations on the physics of crystals, which I and my collaborators have been carrying on for the last twenty-five years. This book presents the content of those lectures. It covers a limited portion of the field of the elastic and electrical properties of solids. In organizing this material, I have attempted to discuss all the various problems from the one point of view which has been the guiding thread of all my work on this subject.

It has been believed that the solid state, because of the close approach of the atoms, ought to be the most complicated of all organizations of matter, involving the manifestation of molecular forces in all their complexity. The experiments performed, because of the apparently contradictory results obtained, seemed to confirm this pessimistic view. In order to characterize this attitude towards the problem it will suffice to mention two typical conclusions. H. Bouasse, who devoted thirty years to a detailed study of the elastic behavior of solids, came to the conclusion that no general laws exist in this domain. Therefore, he concluded that, in order to give a precise description of the elastic properties of some sample of material, this particular sample must be studied. In the domain of electrical properties of materials, the variety and inconsistency of the experimental data were described by E. v. Schweidler in a paper which he entitled "The Dielectric Anomalies." This title in itself is a sufficient proof of the lack of an explanation.

In spite of such results and opinions, which do seem hopeless, we must remember that the typical simplest representative of the solid state—the crystal—is characterized by the highest degree of regularity, not only in its external shape, but also in its internal structure. Thus it is conceivable that such regularities might lend themselves to study, calculation, and generalization in a new simple fashion. It is, of course, true that in the

close packing of atoms in a crystal there is present a high degree of mutual interaction of the atomic force fields, which is almost absent in rarefied gases. But all atoms of a crystal are in the same relative position and all are, therefore, influenced in exactly the same way. While the structure and properties of an individual atom are distinctly changed by the fields of neighboring atoms, the atoms in such a crystal are all identical, though different from the isolated gaseous atoms. From this point of view, the structure of a crystal looks even simpler than that of a gas for it is a regularly arranged system of identical units, while the states of the various atoms in a gas are all different. The only difficulty encountered in a study from this viewpoint is due to the heat movement which displaces the units and thus subjects them to varying fields. We know, however, that at low temperatures the irregularities brought about by the heat motions vanish rapidly with the decreasing heat energy. At temperatures which are very low but still within the limits of convenient experimental attainment, the heat movements practically disappears completely. The remaining heat agitation must be regarded as a movement of large groups containing a great number of individual units. The mutual position of atoms inside each group is, therefore, constant and regular.

Besides the irregularities produced by heat motions, the real crystal may possess some irregularities introduced during the process of crystallization. It is then a question as to how closely the complete regularity to be expected in the ideal crystal may be approached. We believe and we will later show that by careful crystallization, crystals may be obtained which are regular to an extent to which the remaining faults do not manifest themselves in any physical phenomenon. The behavior of such crystals coincides with the behavior to be expected from the ideal crystal. A crystal as a system of identical units in identical mutual positions ought, thus, to be as simple, if not more so, than a rarified gas. Each property of the crystal is a manifestation of the unit enlarged by the number of units composing the crystal.

Our knowledge of the structure of crystals, which in the past was drawn chiefly from their external shape and from optical data, has been fairly well completed during the last fifteen years by the methods of X-ray analysis. Based on the detailed knowledge of the arrangement of atoms from X-ray data and on Bohr's

model of an atom, an electrical theory of crystal lattices was developed by M. Born, which gave an adequate picture of the crystal. Since this time we have a model which guides us in looking for the mechanism of the phenomena observed in crystals and in predicting new properties. We shall make extensive use of this model in the discussion and explanation of experiments which follow.

The experimental study of crystals has as its purpose not only the proof of the theory, but the object of transforming it from a mathematical scheme to the physical model of a real body. In the course of the lectures we shall see that all of the phenomena which seemed to contradict the fundamental assumptions of the electrical theory of crystals turn out, on a closer investigation, to be no contradiction at all. We may state that the basic features of the theory actually represent the behavior of crystals, both qualitatively and quantitatively.

On the other hand, we shall notice that many phenomena actually observed, while not contradicting the theory, are not completely explained by the theory. They indicate the necessity of an additional more detailed development of the theory. In achieving a more concrete form of the model, the theory must be guided by the properly formulated experimental results.

One of the important results of the experimental study here presented is the possibility of extending the experiments far beyond the limits of previous studies. By investigating the phenomena which limit the scope of the experiment, we find out their mechanism and thus learn to avoid or reduce the causes of those limitations. We find, for instance, that the scope of the elastic forces studied may be extended about five hundred times beyond the usual limit of rupture, and in the study of electrical fields we find that the electric fields in sufficiently thin sheets may reach three hundred times the value usually producing electrical breakdown.

Thus, while we were previously limited to elastic and electric deformations so small that they were represented by terms of first order only—corresponding to Hooke's law, and Ohm's law—we are now able to attack the problem of the atomic forces in the general form which also includes the large deviations. It is to be expected that many obscure points of the electrical theory may be cleared up by the field of investigations which has been thus enlarged. We may, in particular, hope to throw some new light upon the origin and laws of the repelling forces between the atoms.

The reader will notice that but a few of the problems may be regarded as solved by the experiments described, and many new problems have arisen. A considerable part of the work is thus still in progress and, therefore, can at this time be presented in a preliminary fashion only. I accordingly believe that the readers' indulgence must be asked for this incomplete state of the subject. It seems probable, however, that, even in this incomplete state, the material here presented may be of some use to those who are interested in the behavior of solids.

I began this work on crystals in 1903, at first in collaboration with W. C. Röntgen, and then with Mrs. M. V. Kirpicheva. Both died in 1923. Since this time, my collaborator in studying the elastic properties was Miss M. A. Levitsky, and on the study of the electrical properties was K. D. Sinelnicov. Several important electrical problems were carried out by P. T. Lukirsky, Alexander F. Walter, Anton K. Walter, T. V. Curchatov, P. P. Cobeco, D. S. Rojansky, Miss S. N. Arsenjeva, Miss N. S. Ussataja, B. M. Hochberg, E. V. Zechnovitzer, N. S. Shucarev, Miss O. N. Trapesnicova, S. M. Venderovich, V. S. Condratev, and A. T. Rabinovich. In the investigation of elastic phenomena, I was glad to have the assistance of P. S. Ehrenfest, Miss M. V. Classen, B. F. Peenes, T. V. Obreimov, and L. V. Shubnicov. Many theoretical problems were carried out by F. T. Frenkel, G. A. Grünberg, and V. R. Brusian.

The results here presented are due to the cooperation of all of us and it is hardly possible to formulate the exact limits of the work of each one. The material has been already partly published. A list of the publications containing this, and the papers mentioned in the lectures as closely connected to the problems discussed, is given at the end of each lecture.

The subject of the lectures may be naturally divided into two central problems concerning the mechanical and the electrical behavior of crystals. The first six lectures present a discussion of the mechanical problems. The last eleven lectures deal with the electrical properties of both single crystals and solid dielectrics. In discussing the two sets of phenomena it was found more convenient to use a new notation for the constants of the second set and to number the formulae and equations anew, beginning with the seventh lecture.

ABRAM F. JOFFÉ.

BERKELEY, CALIFORNIA
June 10, 1927

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INTRODUCTION

Those of us who had the pleasure of hearing Professor Joffé's lectures at the University of California have eagerly awaited their publication in book form, that we may renew, and that others may make, acquaintance with this remarkable record of experimental research.

In late years the great rush to the new gold fields of physics has caused a temporary abandonment of the well worked but still rich leads of classical physics. The author has returned to one of the most old-fashioned of physical themes in his study of the mechanical and electrical properties of solids, and in this rejuvenation of an ancient problem with the aid of all modern resources of theory and practice, our admiration is divided between the ingenuity of the methods devised and the technical skill shown in their application.

Each of the problems that Professor Joffé has solved has suggested other unsolved problems of great theoretical and practical importance to physics and chemistry. The barriers between these two sciences are being steadily demolished and this volume is sure to arouse an equal interest among physicists and chemists.

GILBERT N. LEWIS.

THE PHYSICS OF CRYSTALS

LECTURE I

ELECTRICAL THEORY OF CRYSTAL LATTICES

Our idea of a crystal is very simple and definite. We regard the crystal as a regular arrangement of small units (atoms, ions, or molecules). A particular mutual orientation or position of the units relative to one another corresponds to a minimum of free energy. This will be the position of stable equilibrium. All units are supposed to be identical. What is true for one of them is therefore true for every other one. At sufficiently low temperatures we may neglect the influence of the heat agitation and consider the equilibrium as a static one.

We believe that the unit of a crystal lattice is a system of electric charges and that no forces are to be expected other than electric and magnetic fields. We might see in a crystal a regular arrangement of smaller units than atoms, to wit, of positive nuclei and negative electrons. We must look for the minimum of energy of the whole system. The dimensions of the electrons and the nucleus are small relative to the distances between them. No more than the 10^{-15} part of the space is occupied by these elements. The crystal, from this standpoint, is an empty space with small charged particles distributed at enormous distances from each other. We believe that the quantum conditions inside the atoms are responsible for the dimensions of the electronic orbits and thus for the uneconomical disposition of space.

Contrary to the conditions inside the atom, where the distances are large relative to the charges, the distance

between the atomic systems in a crystal lattice is of the same order of magnitude as the atoms themselves. The arrangement of atoms in a crystal lattice corresponds to a very close sort of packing. The position of static equilibrium of the atoms seems to follow from the forces calculated by classical electrodynamics without the intervention of quantum conditions.

The problem of the equilibrium of forces in a crystal lattice might be expected to be very complicated. To study this problem, we may proceed to consider it under the following heads:

1. The purely electrostatic forces between the atoms. Of course we must remember that the charges producing the electrostatic fields are moving and their fields are, therefore, periodic functions of time and space. Two cases must then be distinguished: (a) the movement of electrons in different atoms are controlled by phase relations. The average forces resulting in this case are considerable and do not correspond to the interaction of the average fields. (b) The independent movement of electrons in different atoms. In this case the *average* action is given by the average fields of atoms.

2. In calculating the fields of atoms, we must consider the change in the distribution of electrons inside the atom produced by the electric field of the surrounding atoms. The unit of a crystal lattice may differ essentially from the same unit in an isolated state as represented by a gas at a low pressure. The action of an electric field on an atom is supported by its electrons. As the connections between the nucleus and the electrons are not rigid, the charges inside the atoms will be displaced by an electric field, and therefore both the field of the first atom and the field of the second will be influenced and changed by the mutual action. This displacement as occurring inside the atoms must correspond to a complicated Stark effect, which may be calculated on the basis of quantum mechanics.

3. Besides the electrostatic fields existing, a system of moving charges which occurs in the atoms may pro-

duce electrodynamic and magnetic forces of a periodic character.

4. We must expect the kinetic energies of the electrons to play an important part in the equilibrium conditions, because a stable equilibrium in an electric system of moving charges has to satisfy the general condition that the average kinetic energy must be equal to half of the (negative) average of the potential energy.

The various phenomena mentioned under (2), (3), and (4) above seem, however, of a secondary importance for the calculation of an equilibrium state of a crystal lattice. As was shown by Born, the pure electrostatic theory of crystal lattices gives an adequate account of the behavior of the crystal. Even the displacement of charges (item (2) above) inside the atoms, which also admits of an electrostatic treatment, may be neglected in many cases. We know, of course, that no stable equilibrium is possible in an electrostatic system of charges producing fields for which the Laplace equation holds. Electrodynamic and quantum relations must, therefore, be responsible for the stability of a crystal.

The simple and reasonable theory of Born leads to a remarkable agreement with the observed phenomena and represents a suitable model of a crystal. From time to time it is necessary to introduce into the calculations empirical data and, possibly, some one of the neglected phenomena above discussed. We will, therefore, use Born's theory of crystal lattices as a basis for the investigation of solids. In doing so, we must remember what phenomena were neglected in the general assumptions of the theory and correct our model if the neglected values become essential.

The electrostatic potential may be represented by the scalar potential φ . The strength of the electric field E in any direction x is then represented by the derivative of φ ,

$$E = - \frac{\partial \varphi}{\partial x}. \quad (1)$$

For a single charge e the potential φ at a distance r from the charge, if the size of the charge be considered as very small compared to r , is

$$\varphi = \frac{e}{r}, \quad (2)$$

and a system of charges produces a potential

$$\varphi = \sum_i \frac{e_i}{r_i}, \quad (3)$$

where e_i are the charges.

Using Taylor's series for $1/r$, we may represent the potential in this form:

$$\begin{aligned} \varphi = \frac{1}{r} \sum_i e_i + S_k \frac{\partial \left(\frac{1}{r} \right)}{\partial x_k} \sum_i e_i \xi_k + \frac{1}{2!} S_{k,l} \frac{\partial^2 \left(\frac{1}{r} \right)}{\partial x_k \partial x_l} \sum_i e_i \xi_k \xi_l \\ + \frac{1}{3!} S_{k,l,m} \frac{\partial^3 \left(\frac{1}{r} \right)}{\partial x_k \partial x_l \partial x_m} \sum_i e_i \xi_k \xi_l \xi_m + \dots \quad (4) \end{aligned}$$

where r is the distance from some point O inside the system to the point A for which the potential is to be calculated; x_1 , x_2 , and x_3 are the coordinates of O referred to A as origin; and ξ_1 , ξ_2 , ξ_3 are the coordinates of the charges e referred to the point O as origin. Σ indicates summation over the different charges, and S indicates summation with respect to the different coordinates ξ_1 , ξ_2 , and ξ_3 . The single terms in this series have a simple physical significance. The first term represents the potential of all the charges placed at the point O . The second term is the potential due to an elementary dipole, which must be a dipole of very small size compared with r . The three moments $\Sigma e \xi_1$, $\Sigma e \xi_2$, $\Sigma e \xi_3$, parallel to the three coordinates, determine the second term. The third term is the potential due to a very small elementary quadrupole. This consists of two opposed dipoles $e \xi_k$ separated by a small distance ξ_l . The fourth term represents the potential of an elementary octopole. This is a system of two opposed quadrupoles, or a cube with alternate charges on the corners. In a similar fashion the other terms may be added.

Let us consider these symmetrical systems of charges separately. We ascertained that by superposing the fields of the elementary systems we can represent the electric field of any system which it is desired to represent.

Case 1. The Single Charge (Fig. 1).—The field is isotropic independent of the direction and dependent on r only,

$$\varphi = \frac{e}{r}.$$

Case 2. The Dipole (Fig. 2).

$$\varphi = \frac{M}{r^2} \cos \alpha, \quad (5)$$

where M is the moment of the dipole equal to the product of the charge and the distance l between the two opposite charges

$$M = el.$$

The field depends on the angle α between the axes of the dipole and the direction of the calculated point. φ is positive for

$$-\frac{\pi}{2} < \alpha < \frac{\pi}{2},$$

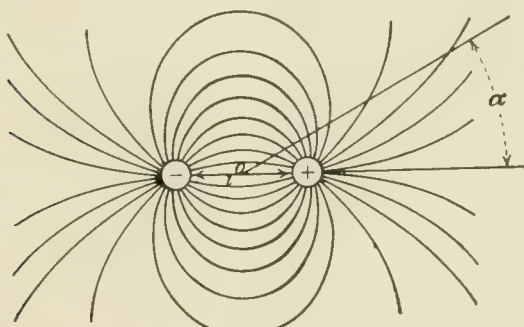


FIG. 2.

and negative for

$$\frac{\pi}{2} < \alpha < \frac{3\pi}{2}.$$

Case 3. The Quadrupole (Fig. 3).

$$\varphi = \frac{3Mm \cos \alpha \cdot \cos \beta}{r^3}, \quad (6)$$

where m is the distance between two dipoles. $N = M \cdot m$ is the moment of the second order of the quadrupole. α is the angle between the given direction OA and the axis l of the two parallel dipoles and β the angle between the same direction and the axis m of the quadrupole. The field changes its sign four times when α and β increase from 0 to 2π . For the same angles α and β the potential is inversely proportional to r^3 , and the field is therefore inversely proportional to r^4 .

Case 4. The Octopole (Fig. 4).

$$\varphi = \frac{3 \cdot 5 N \cdot n \cdot \cos \alpha \cdot \cos \beta \cdot \cos \gamma}{r^4} \quad (7)$$

$O = N \cdot n$ is a moment of the third order. The field changes its sign eight times in the eight divisions of the space. The potential is inversely proportional to r^4 , and the field is inversely proportional to r^5 .

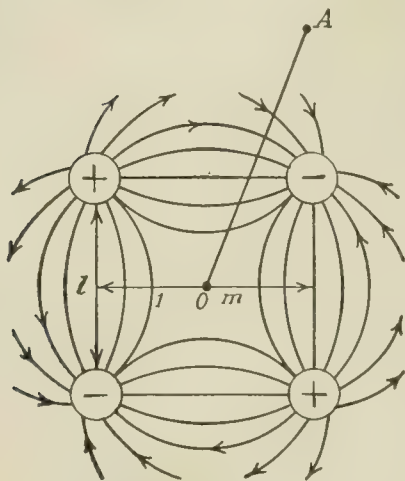


FIG. 3.

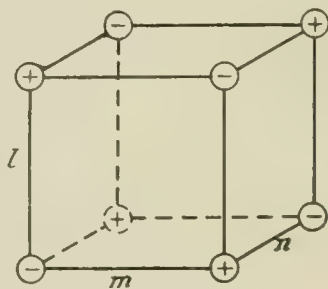


FIG. 4.

5. A system of 8 positive charges at the center and of 8 electrons at the corners of a cube surrounding the positive charge represents the next symmetrical case of 16 charges, or of 8 dipoles. The potential of such a system is inversely proportional to r^5 , and the field is inversely proportional to r^6 .

We conclude that the higher the degree of symmetry, the higher is the power of r . This signifies that the field in

these cases decreases more rapidly with the distance from the system. Graphically, the potential of the systems considered may be represented by Figs. 5 and 6, where φ is represented as a function of r and α , respectively.

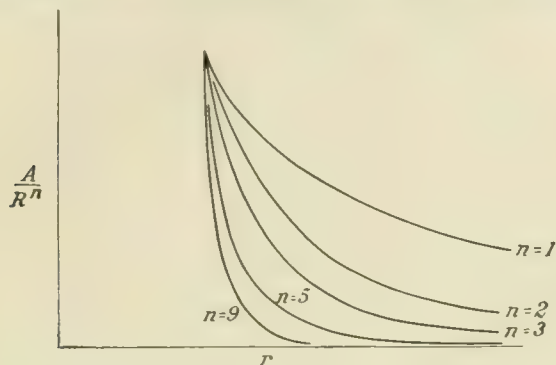


FIG. 5.

The problem we have in the case of a crystal lattice is the study of the mutual energy and the force between the electrical systems. The potential energy of a system of charges in a field of the scalar potential φ may be represented by

$$u = \varphi \sum e + S \frac{\partial \varphi}{\partial x_k} M_k + \frac{1}{2!} S \frac{\partial^2 \varphi}{\partial x_k \partial x_l} N_{kl} + \dots \quad (8)$$

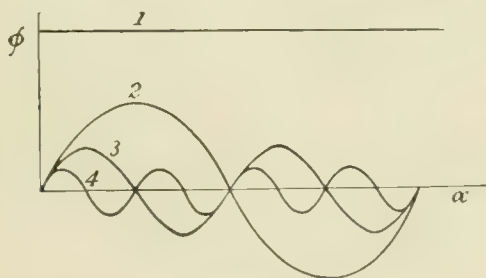


FIG. 6.

If we replace our system by the sum of the elementary symmetrical systems, we may represent the energy as a sum of terms such that the first term gives the energy of the charges as if they were concentrated in one point.

The second term depends on the first derivative or the gradient of the potential and gives the energy of the elementary dipole placed at the same point; the third term gives the energy of an elementary quadrupole and so on.

If the field is due to a second system of charges, we must replace φ by its value as given in equation (4). We then obtain a double sum that may be expanded into a power series in $1/r$, *i.e.*,

$$u = \frac{C_1}{r} + \frac{C_2}{r^2} + \frac{C_3}{r^3} + \dots \quad (9)$$

where C_n/r^n is the sum of all terms containing $1/r^n$. The first coefficient is

$$C_1 = \Sigma e \times \Sigma e',$$

where e' represents the charges of the second system. The second coefficient is

$$C_2 = M \cos \alpha \Sigma e' + M' \cos \alpha' \Sigma e,$$

where α is the angle between the axis of the moment M and the line connecting the two systems, and α' the angle between the moment M' of the second system and the same line. The calculation of the other terms becomes more and more complicated, but does not, in principle, present any difficulty.

Equation (9) represents the mutual energy of two electric systems, such as two ions composing a heteropolar molecule or two atoms of a homopolar molecule.

In a crystal lattice, we have each unit surrounded by a number of other units. In a heteropolar crystal each positive ion has around itself several negative ions. For a lattice of tetrahedral type (ZnS) there are four such opposite ions, in a lattice of a cubical type (NaCl), six ions, and in a lattice of the type of CsCl, eight ions. This shell of opposite ions is then surrounded at a greater distance by a second shell of ions of the same sign as the inner ion. For systems of a high degree of symmetry, the potential and the forces diminish as a high power of the distance, so that the second and third shells give but small corrections to the

effect of the first shell. It is different for ions producing a potential that is inversely proportional to the distance.

Madelung has computed the potential energy, adding first the energy of all ions in the same line, then the mutual energy of all lines in one plane, and finally the energy of all the planes in a crystal. Ewald developed a more general method, representing the electric fields by exponential functions. As a result of such calculations, we find that the potential energy of an ion in a crystal lattice may be represented by

$$u = k \frac{e^2}{r}$$

if we regard the ions as point charges e distributed at distances r . The coefficient k depends on the kind of the crystal lattice and does not depend on its dimensions or the magnitude of charges. For a tetrahedral lattice (ZnS), we may compute

$$k = 1.64;$$

for a cubic lattice (NaCl)

$$k = 1.75;$$

and for a lattice of the most symmetrical double cubic kind (CsCl), we obtain

$$k = 1.76.$$

For the whole crystal consisting of N positive and N negative ions, we find

$$U = N \cdot u = \frac{Nke^2}{r}.$$

It may be remarked that we have to multiply by N and not by $2N$, the total number of ions (both positive and negative), because equation (9) refers to the mutual energy of the positive ions and the negative ions. The result uses each energy only once. N may be regarded as the number of diatomic molecules in the crystal. The value of k does not hold for the ions of the surface layer, as they are not surrounded symmetrically by the opposite ions. The potential energy of these ions is therefore greater than for the ions inside the crystal. The difference

of these energies for the ions per cm.² of the surface gives the surface tension of the crystal.

It is obvious that the surface tension depends on the orientation of the surface. This dependence is responsible for the external shape of a crystal.

Equation (8) gives the energy of a system in an electric field. The corresponding mutual forces follow from the general relation

$$f_x = -\frac{\partial U}{\partial x}.$$

We must remember that the charges are not bound absolutely rigidly but occupy the positions corresponding to some equilibrium of the electric and electrodynamic forces. If a new set of forces f_x originating from another system appear, the equilibrium positions of charges will be changed. Thus, new moments of different order will be produced. The first derivatives of the potential φ produce the dipole moment, the second derivatives are responsible for the appearance or change of the quadrupoles, etc. The deformation of the system so obtained decreases the mutual potential energy U of the systems by $-\Delta U$. At the same time the internal energy of the deformed system, *i.e.*, the mutual energy of charges inside the same system, increases by $\Delta U'$. It can be shown that

$$\Delta U' = -\frac{\Delta U}{2} \text{ (Theorem of Virial),}$$

so that the actual decrease of the potential energy is equal to

$$\frac{\Delta U}{2}.$$

The deformation of the units of a crystal lattice has never been completely calculated. The dipole moments only have been taken into account in calculation, using the moments produced in the same units by the electrical field of light waves as measured by the coefficient of refraction. While the electric field of light waves is periodic in time, it is uniform in space for atomic systems of dimensions

10^{-8} cm. Therefore no moments of higher order can be affected by light. The conditions are obviously different for the atomic field in a crystal lattice where these moments become predominatingly important. The calculation of the mutual polarization will usually represent, therefore, but a rough approximation.

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LECTURE II

EQUILIBRIUM IN A CRYSTAL LATTICE

The electrical theory of crystals has been practically reduced to an electrostatic theory in spite of the fact that the electrostatic model of the atom has failed. For the atom we are using an electrodynamic model developed by Bohr. It might be of interest to estimate the magnitude of the neglected electrodynamic phenomena.

We have neglected the influence of the mutual energy on the kinetic energy of the electronic movements inside the atoms, for we consider their displacement only. As the average potential and the average kinetic energy are connected, and as we do not compute the displacement from electrostatic forces, but from the actually observed polarization, the influence of the kinetic energy seems to be taken into account as far as the moments of the first order are concerned, and we need not consider this point further.

We have, furthermore, neglected the electrodynamic fields, which seem to be the characteristic feature of Bohr's atoms. A rough calculation of the order of magnitude of these fields, however, justifies Born in neglecting these forces, as may be seen below. In order to compare the magnitude of forces due to electrostatic fields with the forces produced by the magnetic field of atoms, assume the distance between the centers of adjoining units in a lattice to be $r = 2 \times 10^{-8}$ cm., the distance between the charges inside a unit being $s = 0.5 \times 10^{-8}$ cm. We then compute the force between two ions with opposite charges $\epsilon = 4.77 \times 10^{-10}$ as

$$f_i = \frac{e^2}{r^2} = 5.7 \times 10^{-4} \text{ dyne.}$$

For two dipoles we obtain in the direction of their axis

$$f_d = \frac{3!M \cdot M'}{r^4} = 2.1 \times 10^{-4} \text{ dyne};$$

for two quadrupoles

$$f_q = \frac{5!N \cdot N'}{r^6} = 2.7 \times 10^{-4} \text{ dyne};$$

and for two octopoles

$$f_o = \frac{7!O \cdot O'}{r^8} = 7 \times 10^{-4} \text{ dyne}.$$

The magnetic moments of the rotating electrons may be represented as small multiples of the Bohr magneton $\mu = 0.92 \times 10^{-20}$. At a distance of $r = 2 \times 10^{-8}$, the force between two magnetons will be

$$f_m = \frac{6 \cdot M^2}{r^4} = 3.2 \times 10^{-9} \text{ dynes}.$$

Even if we take the highest number of the Bohr magnetic quanta known to exist, that is, about 20, the force is:

$$f_m = 1.28 \times 10^{-6},$$

about two hundred times as small as the electrostatic forces. These we may now consider more closely.

The electrostatic theory gives the potential energy of a crystal lattice as a power series in $1/r$

$$U = \frac{C_1}{r} + \frac{C_2}{r^2} + \frac{C_3}{r^3}. \quad (9)$$

The negative terms in this series correspond to attractions; the positive terms give the energy of repulsive forces. Both kinds of forces are necessary in a model of a crystal. Without the attraction between the units of a crystal, it would disintegrate. Without a repulsion between the units they would coalesce. Elasticity, heat expansion, diffusion, and electrical conductivity show, however, that some free space must exist between the atoms; and this is impossible in a model without mutual repulsion. At least two terms, one negative and one positive, must accordingly be present in equation (9). In a normal state without external forces, the internal energy must reach

the minimum value and the mutual attractive and repulsive forces must become equal. We may even go further. It is obvious that, for stable equilibrium in an expansion of the crystal as a whole, the attractive forces must predominate between the units, while in a compression the repulsive forces between the units must predominate. Thus, the repulsion must decrease more rapidly than attraction when the distance is increased, and must increase more rapidly than the attraction when the distance is decreased. We may, therefore, conclude that in our power series in $1/r$ (equation (9)), the attraction must be represented by terms with a lower exponent than the repulsion; and as will be shown, this leads at once to the necessary condition of a stable equilibrium, namely, that the resulting attraction must increase with the distance,

$$\frac{df}{dr} > 0.$$

Our experimental knowledge of crystals is limited to very small changes in r . Therefore it would be useless to choose for the energy an expression with a great number of unknown coefficients such as the series of equation (9). We may, therefore, satisfy the experimental data using the smallest number of terms, namely two, one for attraction and one for repulsion.

$$U = -\frac{A}{r^m} + \frac{B}{r^n} \quad (10)$$

For the normal distance r_0 the energy U must be a minimum and

$$\frac{dU}{dr} = 0. \quad (11)$$

The forces following from equation (11) are

$$f = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}}. \quad (12)$$

In the normal state, $f_0 = 0$ and

$$\frac{mA}{r_0^{m+1}} = \frac{nB}{r_0^{n+1}}; \text{ or } nB = mA r_0^{n-m}. \quad (13)$$

Using the relation in equation (13) we may represent the energy by

$$U = -\frac{A}{r^m} \left[1 - \frac{m}{n} \left(\frac{r_o}{r} \right)^{n-m} \right], \quad (14)$$

and the force by

$$f = \frac{mA}{r^{m+1}} \left[1 - \left(\frac{r_o}{r} \right)^{n-m} \right]. \quad (15)$$

For $r = r_o$ we have

$$U_o = -\frac{A}{r_o^m} \left(1 - \frac{m}{n} \right). \quad (16)$$

If $f_o = 0$, then

$$\left(\frac{df}{dr} \right)_o = \frac{mA}{r_o^{m+2}} (n - m). \quad (17)$$

Thus, it is seen at once that the condition that $\frac{df}{dr}$ is positive in a stable equilibrium leads to the result that n must be greater than m , or

$$n > m. \quad (18)$$

Figures 7 and 8 express the conditions given by the equations (10) to (18) graphically.

Assuming the approximate equation (10) we express the energy U by five quantities: A , B , m , n , and r , satisfying one relation in equation (13) and the inequality in equation (18). For the determination of these quantities we may use the following: (1) X-ray analysis giving the value of r_o ; (2) The measurements of the heats of dissociation and sublimation, leading to the value U_o ; and (3) the compressibility κ_o whose relation to the quantities A , m , n , and r_o may be found from the definition of κ , viz.,

$$\frac{1}{\kappa} = V \frac{dp}{dV}. \quad (19)$$

Here the volume $V = Nr^3$, if N is the number of elementary cells in the crystal. The pressure p may be derived from the energy by the relation

$$p = -\frac{dU}{dV}; \quad \frac{dp}{dV} = -\frac{d^2U}{dV^2}. \quad (20)$$

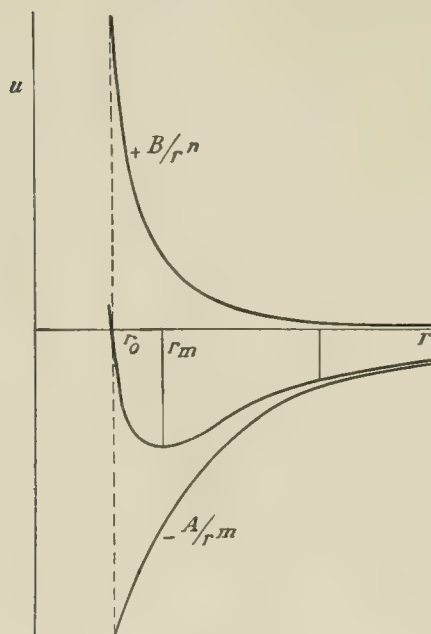


FIG. 7.

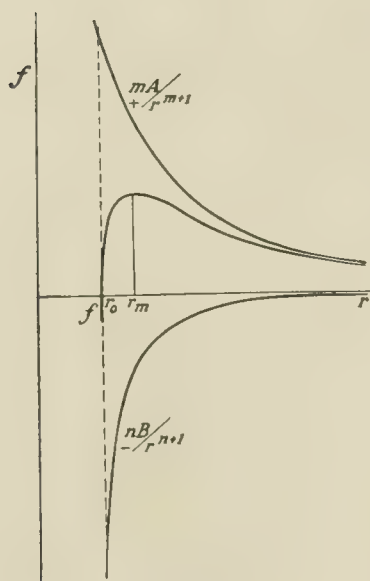


FIG. 8.

For the normal distance r_o , we have then

$$\frac{1}{\kappa_o} = -V \left[\frac{d^2 U}{dr^2} \left(\frac{dr}{dV} \right)^2 + \frac{dU}{dr} \frac{d^2 r}{dV^2} \right] = \frac{-1}{9V_o} \frac{m(n-m)A}{r_o^m} \\ = -\frac{m \cdot n}{9} u_o, \quad (21)$$

where $u_o = \frac{U_o}{V}$ is the potential energy of a cm.³ of the crystal.

Knowing m from the expected degree of symmetry of the units of the crystal lattice we are able to compute A , B , and n , using the measured values of r_o , u_o , and κ_o . For heteropolar cubic lattices, for instance, we know both that $A = Ke^2/r_o$ and $m = 1$. Equation (21), which now has the form,

$$\frac{1}{\kappa_o} = \frac{n-1}{9} \times \frac{A}{r_o}, \quad (22)$$

gives the value of n . Using equation (13) we obtain B .

Equation (16) allows us to compute the energy. We see that the energy is mainly given by the attractive term $-\frac{A}{r^m}$, while the repulsion affects u_o as a correction that becomes small for $n \gg m$.

The fact that the computed value of u_o agrees with the results of heat measurement yields a satisfactory proof of the electrostatic theory. The values of n obtained from the bulk modulus are consistent with the degree of symmetry assumed for the units of the lattice. For the heteropolar lattices, if we identify the units with ions, and assume for the ions the structure of the corresponding neutral gases, suggested by Prof. Gilbert Lewis, we might expect n to be equal to 9. In fact, we get for ions of the Argon type $n = 9$ and for other ions $n = 10$ or 11 . We get less than 9 for the less symmetrical ions corresponding to He.

Assuming equation (10) instead of equation (9), we may replace the series corresponding to attraction and repulsion by the first term which is essentially different from zero. If this term represents the energy, it, and its first and second

derivatives for distances greater than the normal distance $r = r_o$, will be of primal importance and it is obvious that the terms of higher order will have less and less influence as r increases above r_o . On the other hand, for values of r which decrease below r_o we must expect the influence of the neglected terms to become more and more pronounced. The study of crystals at high pressures and low temperatures may, therefore, give some useful data for the development of the theory of crystal lattices.

Using the representation of the energy of a crystal by equation (10), we may distinguish the following types of crystal lattices:

1. *Heteropolar Lattices*.—Such lattices have $m = 1$, $n = 9 - 11$ for the most symmetrical ions of the neutral gas type. n would be 5 if one of the ions were replaced by a point charge such as an electron or a nucleus. The suggestion made that we consider the metal as a heteropolar lattice of positive ions and negative electrons, and the lattices of the halogen acids as a lattice of negative ions and positive nuclei has not been checked by experiment. Accordingly we do not now know of any real crystals corresponding to such a model.

2. *Metals*.—The most probable model for a solid metal seems to be a lattice of positive ions with negative electrons moving in orbits of such an irregularity that they may be considered on the average as a negative fluid spread continuously over the whole space between the ions. This model leads to the equation approximated by equation (10), taking $m = 1$, $n = 3$.

3. *Dipole Lattices*.—In this case $m = 3$, $n > 3$. We have some evidence that the crystals of halogen acids are of this type. The calculation requires, however, a consideration of the mutual polarization of the dipoles.

4. *Molecular lattices* of neutral units of higher symmetry such as the diamond. The magnitude of the attractive forces produced by the quadrupole moments of carbon atoms might be sufficient if some favorable mutual orientation of atoms is assumed. This orientation must hold

continuously and requires that some very definite phase relations between the electrons moving in different atoms through the whole crystal exist. Without such phase relations we would have attraction and repulsion occurring with almost the same probability. Such a model thus becomes too artificial and too sensitive to the particular shape of electronic orbits. Our knowledge of these orbits seems to be insufficient to give us a proper basis for the calculation of the lattice. In spite of the good numerical results obtained in the computations of Frenkel, we may expect that the model will be changed in the future by new experiments.

The case of the complicated organic compounds seems to be more simple. The units of the lattice are represented by large molecules with a distribution of charges following from stereochemical data. On the basis of these data we may compute the attraction term and, proceeding in the above described manner, get the values for A , B , and n .

While we use an analogous system of representation for attracting and repelling forces, we must state a fundamental difference between the assumptions of this sort for the two cases. The energy of mutual attraction, assuming that we may neglect terms of higher symmetry, may be deduced directly in the cases of heteropolar and dipolar lattices from the nature of the forces. Accordingly, the potential energy of the crystal calculated from the electrostatic theory of attraction, with a small correction due to repulsion, agrees with experimental data and checks the theory in a satisfactory way. The contrary may be said concerning the repulsive forces. They are unknown in their detailed action. The above mode of calculation would give results of reasonable magnitude for the mutual repulsion if we were using a static atom model with electrons at rest. For an actual model with electrons moving in quantum orbits, the average force calculated is too small. On the other hand, no phase relations can be assumed to increase these forces, because no synchronous movement can exist between electrons in atoms of different chemical

natures, such as, for instance, the sodium ion and chlorine ion. We are therefore obliged, assuming that the energy of repulsion may be expressed by B/r^n , to compute the values of B and n from compressibility measurements and the measurements of atomic distances as was stated before. It is a satisfactory feature of our atomic models, that the value of the exponent n obtained in this way agrees fairly well with the exponent n that might be expected from the degree of symmetry of the ions producing the repulsion, but it does not explain the mechanism of repulsion.

Possibly the major portion of the repulsive forces cannot be explained by the purely electrostatic fields of atoms. At least we do not possess at this time a satisfactory theory of repulsion in crystals. The term B/r^n , representing the energy of repulsive fields, may therefore include some phenomena other than electrostatic.

In some cases, equations (9) and (10), containing central forces only, were shown to be inadequate. It is then necessary to use a more complicated law of force taking into account the mutual orientation of ions.

No matter what kind of electric forces may act and what formula we must use, the general shape of the curves representing the dependence of U and f on the size of the atomic cells and on the size of the crystal, must correspond to Figs. 7 and 8. Thus, the force resulting from attraction and repulsion must be zero at the normal distance r_0 , must become positive on expansion and negative on compression. The resulting force must increase more slowly with the distance in the first case than in the second.

At some value of the expansion the pressure reaches a maximum negative value. Thereafter it decreases in magnitude approaching zero asymptotically. The distance r_m , corresponding to this maximum pressure, and the maximum expansion possible in the crystal may be found by putting

$$\frac{dp}{dV} = 0.$$

Using equation (20) for dp/dV and equation (14) for U , we obtain

$$\frac{r_m}{r_o} = \left(\frac{n+3}{m+3} \right)^{\frac{1}{n-m}}; \quad (23)$$

and for the maximum pressure p_{\max} ,

$$p_{\max} = - \left(\frac{dU}{dV} \right)_{r=r_m} = \frac{m(n-m)}{3V_o \times r_o^m} \times \frac{A}{n+3} \left(\frac{m+3}{n+3} \right)^{\frac{m+3}{n-m}}. \quad (24)$$

Using equation (21), we may write

$$p_{\max} = - \frac{3}{n+3} \left(\frac{m+3}{n+3} \right)^{\frac{m+3}{n-m}} \times \frac{1}{\kappa_o}. \quad (25)$$

Applying equations (23) and (25) to a crystal of rock salt, we may use $m = 1$, $n = 9$, and $1/\kappa_o = 2.4 \times 10^{11}$. We then obtain, for the maximum uniform dilatation, the change in linear dimensions expressed by

$$\frac{r_m}{r_o} = 1.15. \quad (26)$$

For the maximum negative pressure p_{\max} , we find

$$p_{\max} = -3.46 \times 10^{10} \frac{\text{dyne}}{\text{cm}^2} = -35,000 \frac{\text{kg.}}{\text{cm}^2} = -350 \frac{\text{kg.}}{\text{mm}^2}. \quad (27)$$

This is the cohesive force that must be exceeded in order to pull the crystal apart.

In what has gone before we have considered the simplest case of a uniform expansion or compression. The solid body is, however, distinguished from a liquid by rigidity or elasticity to shearing stresses, which do not exist in fluids. The electrostatic theory also takes account of the stable equilibrium with respect to a shearing strain and permits us to express all the constants of elasticity in terms of the elementary data. In the general case of the least symmetrical type of crystals, the elastic properties may be described by 36 constants, 15 of which may be eliminated by energy equations. The remaining 21 constants are different in the general case. For the most symmetrical cubic type of crystals, this number is reduced to three. The first attempt at an atomic theory of elasticity, developed by Cauchy, failed, however, to give

the total number of constants. This introduced supplementary relations not checked by experiment and led in the general case to 15, and for cubic lattices, to 2 constants only. Born showed that the Cauchy relations hold only for lattices built up of single units. For more complicated cases of a crystal representing many simple lattices put together, Cauchy's relations are not satisfied. Experimental tests checked Born's explanation of this most important contradiction in the atomic theory of elasticity. The numerical agreement is not as close as could be hoped for, only because we do not possess all the necessary atomic data needed for an exact numerical calculation.

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LECTURE III

THE ELASTIC AFTER-EFFECT

The electric theory of crystal lattices furnishes a picture of an elastic body which is, to some extent, similar to the properties of solid crystals. The actual behaviour of solids is, however, much more complicated than this scheme leads one to expect. Some of the experimental results seem to contradict the fundamental idea of a crystal as an equilibrium state of solid matter. We must explain these contradictions by investigating their mechanism in detail.

We may first consider the phenomena occurring within the elastic limit, corresponding to small deformations. From the very outset we encounter a difficulty in explaining the elastic after-effect common to every solid body in a greater or less degree. A stress applied to any ordinary solid body produces a strain continuously increasing with time. Using sensitive methods, we may notice a sort of creeping following a large initial deformation sometimes months after the force has been applied. On removal of the stress, the main part of the strain disappears with the velocity of sound, but some permanent set remains and disappears slowly, the body reaching asymptotically the initial condition. After a sufficiently long time the body recovers completely and no permanent set can be observed. If, therefore, we produce a deformation with an infinitely small velocity, we obtain a reversible process. For a finite velocity the deformation is irreversible and results in a dissipation of energy. For a repeated closed process, the elastic after-effect will lead to an elastic hysteresis. Vibrations will die out more rapidly as a result of the elastic after-effect and the sound emitted becomes dull, etc. Lord Kelvin found that as the vibrations continue, the decay of

vibrations becomes more and more pronounced, and called this an "elastic fatigue." A recovery is to be noticed after a period of rest or on heating. Thus, a wire becomes fatigued by vibrations and recovers on being left to itself for some time.

Analogous anthropomorphic expressions may be used for the after-effect, reminding one in many ways of the human mind. In fact, according to the statement made above, the size and shape of a solid body is no longer a single valued function of the external forces as our reasoning would require, but depends on the whole preceding history. Each stress exerts an influence that dies away very slowly. In a given state we meet traces of stresses which ceased a long time back, but remnants of which are still active at the present.

It would be hopeless to look for an explanation of phenomena like those described above as long as we consider a regular crystal lattice. We may notice, however, that such phenomena have never been investigated in single crystals. The material usually studied consisted of an aggregate of small crystals of a great complexity and irregularity. As was pointed out by Maxwell, such materials may show phenomena like internal friction or after-effect. In fact, the greatest after-effects were found in the most irregular bodies such as rubber, wax, silk, etc. The effect is considerably smaller in metals and in glass and smallest in quartz fibers. The question arises whether or not the heterogeneity is the only cause of the after-effect. Will not a regularly built single crystal be completely free of any after-effect?

I chose for this investigation quartz, because it is readily obtainable in convenient sizes. Its elastic limit is high, and up to a breakage no plastic deformation can be noticed. Its hardness and transparency allow a reduction of experimental errors. Finally I was led to study quartz by a problem, suggested by Röntgen for my doctor's thesis. The problem was whether the stress or the strain is to be considered as the primary cause of piezoelectricity. In

case we should observe piezoelectricity appearing on the surfaces of a quartz plate during an after-effect, we must ascribe it to the strain, because the load, and consequently the stress, does not change. Were the stress responsible for the piezoelectricity, charges must appear at constant strain caused by the disappearance of the stress. The considerations discussed above made the existence of an after-effect in quartz crystals questionable. I thus began with measurements of the magnitude of the possible elastic after-effects in quartz.

In the first experiments, I used piezoelectricity for the measurement of the after-effect. A thin plate of quartz cut perpendicular to a piezoelectric axis, with the main axis in the direction of the width, was provided with silver electrodes and loaded. The electrodes were separated from the earthed ends by narrow insulating strips, as shown in Fig. 9.

One of the electrodes was earthed; the second one, after being earthed for a short time during the loading, was then insulated and connected to an electrometer. The small charge appearing in the electrometer could be easily accounted for by the leakage from the uncovered strips of quartz, serving to insulate the electrode from the end supports. The length of the electrodes was about 80 mm. and the width of the insulated strips was about 0.1 mm. each. Assuming that half of the charge produced by loading will flow to the electrode, we may expect that about 0.1 per cent of the charge produced on the electrode by the same load would reach the electrode in this fashion. The accuracy of the method was about 0.1 per cent and such were the observed deflections of the electrometer. Assuming that if an after-effect were present it would produce charges in just the way an elastic strain does, we may therefore conclude that in the investigated plate no after-effect can exist higher than 0.1 per cent of the deformation.

The piezoelectric method is limited to a definite crystal and a definite crystallographic orientation. Furthermore,



FIG. 9.

the method contains an hypothesis which is reasonable but is not proved. I, therefore, resorted to a more general method, which permits of a higher accuracy. I measured the flexure of a plate supported on two prisms. In order to exclude the displacement of the edges of the supporting prisms and the deformation of the whole apparatus, I measured the change in the distance between the bent quartz plate and a glass plate resting by means of three screws on the quartz plate. The arrangement is shown on Fig. 10. Monochromatic sodium light was reflected both from the lower surface of the glass plate covered with a semitransparent silver layer and from the upper surface

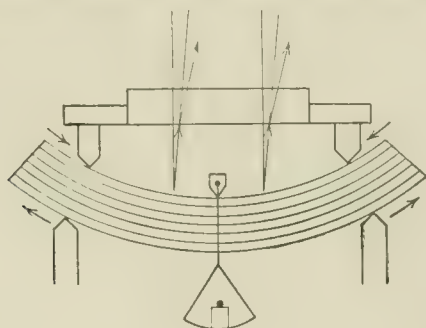


FIG. 10.

of the quartz plate to give interference fringes. If the quartz plate be bent slowly, the fringes will travel. Each time that the distance between the two plates increases by half a wave length of the Na-light used, a given dark fringe will be replaced by the next succeeding one. The position of the fringes relative to a cross-hair in the eye piece was observed from time to time and the progress of the deformation measured.

The first plate used was the same piezoelectric plate as described above. The total flexure was about 1,000 fringes (500 wave lengths). Contrary to what was expected, a slowly progressing deformation was noticed exceeding the accidental experimental errors. Before we can ascribe the observed bending to an after-effect we must consider the

possible systematic errors produced by secondary phenomena. Such phenomena are predicted by the second law of thermodynamics.

The heat expansion requires that every change in dimensions produces a secondary change in temperature, diminishing the deformation. While the temperature change disappears, the deformation progresses from the initial adiabatic value to the final isothermal one. Thus, a phenomenon simulating an after-effect will be produced. The difference between the isothermal modulus S and the adiabatic one δ is given by

$$S - \delta = J \frac{a_1 a_2 T}{\rho C_v},$$

where a_1 and a_2 denote the two coefficients of heat expansion in the direction of the main axis and perpendicular to it; T , the absolute temperature; J , the mechanical equivalent of heat; ρ the density; and C_v the heat capacity at a constant volume.

For the case of quartz we find $\frac{S - \delta}{S}$ to be 0.0021.

A total flexure of 1,000 fringes will produce a thermal secondary deformation of 2.1 fringes. Calculating the velocity of this deformation, however, we find that it cannot be responsible for the observed after-effect. In fact, a bending of a plate compresses the upper layers and extends the lower layers of the quartz plate. The first will be heated, the second cooled. A temperature difference of $2.5 \times 10^{-20}^\circ\text{C}$. between two surfaces appears during the deformation producing a temperature gradient through the plate. Computing the process of the equalization of the temperature by heat conduction in the plate, we find that the remaining gradient, and therefore the remaining deformation, drops down to 1 per cent of the effect during the first 0.07 sec. The recorded movement, however, begins after this time. The thermal effect remaining after this is negligible and falls within the limits of accidental errors.

Besides the secondary heating effect, a deformation of a piezoelectric crystal must also produce secondary electric effects. A calculation on the basis of the second law of thermodynamics determines the electric deformation as 0.9 per cent of the initial deformation, which amounts to 9 fringes for a flexure of 1,000 fringes. The low electric conductivity of quartz leads one to expect that the secondary electric deformation will disappear considerably more slowly than the thermal one. As a matter of fact, a charge insulated by quartz takes days to disappear.

We may easily picture the distribution of charges in a bent quartz plate. Let us divide the plate into a great number of imaginary longitudinal thin layers (Fig. 10).

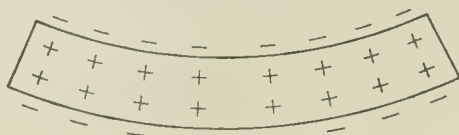


FIG. 11.

The upper layer will be the most compressed. From then on, the compression decreases, becoming zero at some neutral layer. It is replaced by an increasing extension as we consider layers nearer the lower surface. Each layer may be considered as a plate which is charged on both surfaces with opposite electrification by the strain. The charge is proportional to the strain. Each boundary between two layers will be charged positively by the first and negatively by the second, but by differing amounts. A differential charge of the same sign, therefore, remains on each boundary surface, filling the whole plate by a space charge of this sign. A charge of the opposite sign and of the same magnitude as the total space charge inside will remain on the upper and lower surfaces of the plate, as shown on Fig. 11. In what way do these charges recombine? The direction perpendicular to the surface (*i.e.*, perpendicular to the main axis), where the highest electric gradient occurs, is the least conducting direction in the quartz. The direction where the conduction is about one

thousand times better is the direction of the main axis, parallel to the width of the plate. The geometrical conditions (the length of the path and the cross-section) are, however, about one thousand times worse for this direction. It might be expected that by making this second direction of discharge of the space charges easier—to wit, by covering the surface by a conducting layer of silver—we may accelerate the recombination of charges after a bending to some extent. This would, therefore, accelerate the corresponding deformation. This expectation was checked but was not convincing enough to demonstrate the electrical character of the whole effect.

It was, therefore, desirable to remove the space charge by a direct and more complete method. I accordingly tried to increase the internal conductivity of quartz by ionizing rays. At this time, such an experiment had been tried by J. J. Thomson, an increase of conductivity being observed. The observed increase of the current by X-rays was, however, shown by Röntgen to be due to a current going around the solid dielectric through the air. It had been believed, especially by Röntgen, that a real increase of conductivity does not take place. The initial observations of the influence of radium rays on the velocity of the after-effect accordingly gave a negative result. I noticed, however, that while bringing radium into the neighborhood of the crystal or removing it has but little effect on the deformation, *the process was accelerated from day to day* by the numerous exposures to radium rays. Study showed that the conductivity increases gradually through the influence of rays over a period of many days, approaching a maximum value, many times exceeding the initial conductivity of quartz.

We will leave the extended discussion of the influence of different rays upon the conductivity of crystals to the later lectures dealing with the electrical properties. At present, it suffices to say that by increasing the conductivity to the highest possible value, I succeeded in greatly accelerating the elastic after-effect and reached a state where

apparently the whole after-effect was accomplished in a measurable time. In this case the total after-effect was equal to the value computed for the secondary electric deformation, namely 7.2 fringes for an initial flexure of 800 fringes. Figure 12 shows the deformation as a function of time at different states of conductivity, the lower curve corresponding to the normal conditions, the highest to the best conductivity, and the horizontal straight line to the calculated pure electric deformation.

The total amount of the observed elastic after-effect in the piezoelectric plate never did exceed the amount of

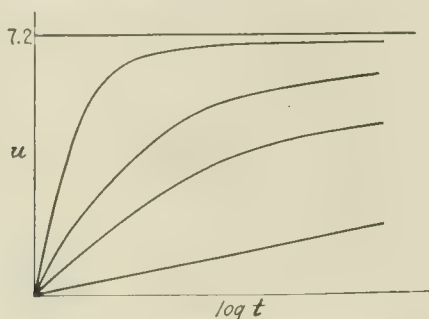


FIG. 12.

the secondary electric effect. The after-effect observed was thus much altered by ionizing rays which could hardly produce a direct elastic effect. In the case where I was able to measure the total effect, it was equal to the electric one. There is, consequently, no evidence for any pure elastic after-effect beyond the expected secondary thermodynamical effect. The limit for the smallest possible real elastic after-effect was, however, not low enough.

I then measured quartz plates having different orientations relative to the crystallographic axes, with the result that the observed effect was always less than the electrical one.

Calculation shows that a crystalline plate cut with the length parallel to the main axis will not produce space charges by bending. In such a plate no secondary electric deformation occurs, and the whole measured after-effect

must be real. *No after-effect was observed in this plate.* The total flexure was increased to 3,000 fringes. Beginning with 1 sec. and during 24 hours after the deformation, no displacement more than 0.1 fringe was observed. The analysis of all possible accidental errors led to a limit of about 0.1 fringe. We conclude therefore that the real elastic after-effect in quartz, if existing, must be less than 3×10^{-5} of the deformation. This is, in fact, quite a low limit if one regards the magnitude of the elastic after-effects usually observed, which go up to 3×10^{-2} and higher values.

This result, obtained in 1904, was checked in 1906 by M. Brillouin, who used quartz springs and ascertained the absence of an after-effect. This property has found an extended application now in the generation of sustained electrical oscillations. Due to the negligible decay of vibrations, piezoelectric oscillators of quartz show an exceptionally sharp resonance for high frequencies.

The result above was then generalized. It was found that single crystals of the metals W, Zn, Cu, and Bi do not show any after-effect within the elastic limit.

Accordingly, the first contradiction to the theory of crystal lattices which we met in the domain of the perfect elasticity is now shown to be no contradiction; for it was found that all disturbing phenomena, such as elastic after-effect, elastic hysteresis, elastic fatigue, etc. do not occur in single, pure, and regularly built crystals. They are due to the irregularities of heterogeneous bodies, to an exceeding of the elastic limit and rupture inside small weak spaces within the body, and to interactions between the crystalline grains.

New difficulties, however, arise as soon as we reach the elastic limit and come into the domain of plasticity.

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LECTURE IV

THE ELASTIC LIMIT

As a result of the study of metals and other aggregates of small crystals, the following statement is usually made about the elastic properties of solids: for the whole domain of perfect elasticity, Hooke's law holds. This means, that, in so far as no permanent set is observed, the strain is proportional to the corresponding stress. A deviation from Hooke's law as above defined, if observed, with the methods used in testing laboratories, indicates an appearance of a permanent set. It is usually assumed that the limit of proportionality may be identified with the elastic limit of the substance. More accurate measurements have, however, shown that deviations from Hooke's law may be observed *before the elastic limit* is reached and that the proportional limit decreases steadily with increasing accuracy of measurements. From the viewpoint which we have taken in the preceding lectures, Hooke's law is nothing more than a neglect of terms of higher order in the force function which was expanded in series in Δr . We may

represent the force $f = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}}$, in the form

$$f = f_0 + f' \Delta r + \frac{1}{2!} f'' (\Delta r)^2 + \frac{1}{3!} f''' (\Delta r)^3 + \dots$$

Assuming $f_0 = 0$, and neglecting all terms containing Δr in a power higher than the first, we obtain Hooke's law:

$$f = f'_0 \Delta r.$$

It is therefore obvious that no proportional limit can be found, because proportionality between the force and deformation is not really expected to exist. The proportional limit observed is a function of the accuracy of the measurement and of the magnitude of the experimental

errors. The very fact that such a quantity had been measured and used in technical tests shows that, before the deviation from Hooke's law becomes evident for rough measurement, a new phenomenon appears producing an essentially permanent set. In other words, a plastic deformation appears at stresses so small that the curve of Fig. 8 does not deviate from a straight line. The elastic properties usually observed in solids correspond to a small fraction of the curve 8 near to the zero point.

Technical tests use a third limit, where an easily perceptible deformation of at least one-half of 1 per cent occurs; this limit is called the yield point. In some multi-

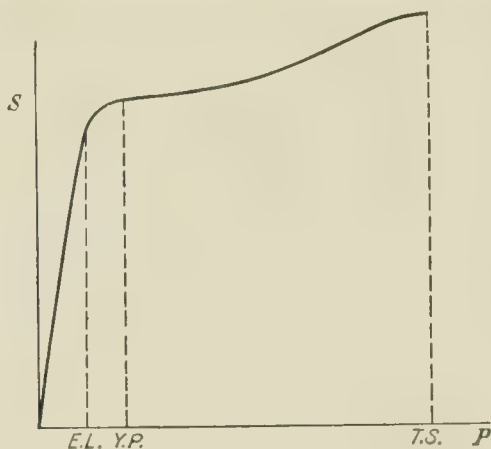


FIG. 13.

crystalline materials, such as iron, the shape of the curve representing the dependence of the strain S of the sample on the tensile stress P justifies such a characteristic. Figure 13 shows a typical curve. The yield point is here more distinctly seen than the elastic limit.

The microscopic investigation of the new phenomenon of a permanent set, causing the elastic limit in crystal aggregates, led to the statement that the permanent deformation consists in a set of small elementary glidings either between the single crystal grains or inside the single crystals. In the first case we observe on a polished surface

large steps in the direction of the maximum shearing stress, *i.e.*, 45 deg. to the axis in a tensile test. In the second case, the slip planes inside the crystals are related to certain definite crystalline planes, such as the base plane in hexagonal crystals, cubic or rhombedodecahedral planes in cubic crystals, which are observable by a microscope only.

One might expect that in studying single crystals we could avoid this complexity of phenomena. Contrary to the elastic after-effect and elastic fatigue, the plastic deformation may be observed, however, in a single crystal such as rock salt, gypsum, zinc, aluminum, etc. The effect is readily perceived when a crystal of rock salt is heated to about 600°C. and bent or twisted. The plasticity of rock salt at this temperature reminds one of wax. Still the bent or twisted crystal remains transparent and seems to form a unit, holding together as firmly as the normal crystal. When released, however, it fails to return to the original form and remains curved. A curved crystal lattice maintained without external forces obviously contradicts the idea of a lattice consisting of an arrangement corresponding to a minimum of potential energy.

We may remark, of course, that a curved external shape is not necessarily bound to a curved internal lattice, since, for instance, we may cut from a normal single crystal a piece of any desirable shape without influencing the internal structure. In fact, assuming that sets of layers in the crystal lattice are moving during a plastic deformation strictly parallel to some crystallographic direction, we would see the crystal lattice still existing when the atoms of the gliding layer come into the same mutual position as in a normal lattice corresponding to a distance of a whole multiple of atomic distances, as shown in Fig. 14.

Thus, an arbitrary permanent set may be produced without change of the normal structure of the lattice. Such a mechanism is perfectly consistent with the lattice theory. Some simple experiments persuade us, however, that the explanation given above does not hold for the actual plastic deformation of crystals. In fact, a deformation corre-

sponding to Fig. 14 would restore the structure of a crystal and return it to normal conditions and, therefore, we should expect in a bent sample the normal properties of a crystal. For instance, the surfaces of cleavage must be plane, following the planes of the regular lattice. Instead of planes we obtain, however, cleavage surfaces curved parallel to the curved external shape of the crystal. This shows that the rock salt has undergone some internal change. On the other hand, as mentioned above, we cannot accept the most plausible picture resulting from the cleavage experiment, namely, a curved lattice without external forces.

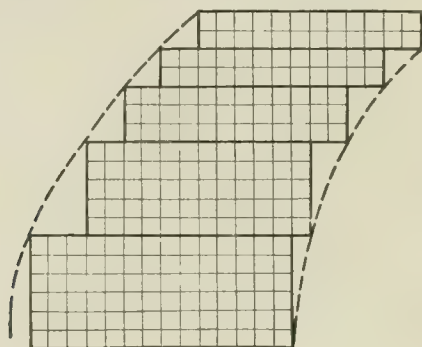


FIG. 14.

Another attempt at an explanation would be to make the internal stresses *remaining* as a result of a heterogeneous deformation of bending or twisting responsible for the curvature. If this explanation is correct, the curvature would decrease when we split a small piece of the bent crystal so that the differences in stresses are small; an experimental test of this was, however, negative. We split a bent crystal of rock salt in two curved parts and heated one part to a temperature of 700°C . during 24 hours. At this temperature the slightest external force exerts a permanent set on the crystal. If internal stresses of such a high intensity as to bend the crystal were present, these stresses must disappear by heating. After careful cooling we brought both parts together and convinced ourselves that

both the external shape and the internal change manifested by curved cleavage did not disappear on heating. While internal stresses are really present in a plastically deformed crystal, they are not the only and even not the main cause of the change in the behavior of the crystal.

The enigma of the plasticity of crystals is, therefore, neither solved by the mechanism of gliding nor by internal stresses.

We ought to know what change in the lattice is actually produced by a plastic deformation. As soon as a method for investigating the structure of lattices by X-rays was developed as a result of Laue's discovery, Mrs. Kirpichewa and I used the method for the study of plastic deformations. We actually found a substantial change in the Laue picture in plastically deformed crystals. Instead of single sharp spots, a picture of radial beams originating from each spot was noticed such as are observed in fiber structures. The explanation of the phenomenon was complicated because of the complicated heterogeneous deformation used.

We proceeded, therefore, to a study of a homogeneous deformation, such as one-dimensional pressure and tension. A uniform pressure easily obtainable by hydrostatic pressure must be excluded as shear is the essential feature of a plastic deformation. In fact, the understanding of the observed phenomena becomes much easier for a uniform deformation. A second important improvement was the visual observation of the Laue picture on a fluorescent screen during the deformation. In a dark room after 10 to 15 min. the sensitivity of the eye suffices to observe the brightest spots of the Laue picture. An ordinary X-ray tube with 70 kv. and 10 ma. was used. The strain corresponding to an elastic deformation could not be observed visually for the tensile test. By taking photographs of a slightly and a heavily strained crystal on the same plate, and using very small holes for X-rays, however, we were able to measure the plastic deformation. A continuous spectrum has to be used for the change in angles, and mono-

chromatic rays for the change in dimensions. Elastic bending and twisting may be observed and easily measured both on a photographic plate and on a fluorescent screen.

For a qualitative investigation of phenomena during a plastic deformation, the visual method has the advantage of showing the whole process and not merely the final result.

On gradually increasing the stress in a crystal we reach some limit at which the Laue picture suddenly changes (Fig. 15). Instead of a system of spots corresponding to reflections from one set of planes in a crystal, one sees several sets of spots superposed in the same picture, which correspond to several crystals. The number of such sets



FIG. 15.

increases while the deformation progresses. All these sets have, however, one spot and consequently one plane in the crystal in common. Thus, the single crystal is seen to be broken into several parts, in spite of the fact that the transparency and rigidity of the resulting agglomeration give the appearance of a single unit. The displacement and rotation of the broken parts corresponds to a slip in a definite crystallographic plane (the 110 plane in the case of rock salt) and a rotation around an axis which is perpendicular to the unchanged plane corresponding to the sharp unchanged spot. This axis may be either perpendicular to the slip plane or may lie in this plane (in the direction of the 100 axis in rock salt, for instance).

The stress at which the first change in the X-ray picture appears corresponds to some irreversible destruction of the

lattice and may be called the destruction limit. Further investigation has shown that the first irreversible slip does not always occur immediately after the limit is reached, and the following slips are separated by time intervals. The measured limit is, therefore, to some extent dependent on the velocity of loading. This error, however, becomes less and less as we go to higher temperatures. Even at room temperature this error may be reduced to 1 per cent for rock salt.

The existence of a definite limit has often been doubted. Experience with metals and glasses led to the opinion that "everything flows more or less slowly." On this basis, a definite limit was considered unlikely. It is, of course, impossible to assert that a body does not flow unless the term "flow" is limited by some minimum velocity. But we can state that at 500°C. not the slightest change in the X-ray picture could be observed after 24 hours if the load is 2 per cent below the measured limit and that at a load exceeding the limit by 2 per cent the change may be noticed within one second. This means physically that the limit has a definite physical value, even if the practically measured value exceeds the theoretical limit corresponding to an indefinitely long time.

We further ascertained that the phenomenon depended on internal stresses and not on the size of the crystal. We chose crystals of the same crystallographic orientation but of different ratios of the cross-section to the perimeter. The limit measured at four temperatures between 20 and 600°C. was always proportional to the cross-sectional areas and independent of the perimeter (Fig. 16). The limit was also the same for compression and tension. Rock-salt crystals of different origin, and consequently with different impurities, and with a surface treated in different ways—for instance, dissolved in water, polished, cleft, etc.—have all the same limit within 2 per cent. We may conclude, therefore, that the destruction limit measured by X-rays has a definite physical significance.

We next investigated the dependence of this limit upon the temperature and found that the destruction limit decreases rapidly with increasing temperature and reaches zero at the melting point, as shown on Fig. 17. Both heteropolar crystals, such as rock salt and sodium nitrite, and metals, such as aluminium and magnesium, were similar in this property. We attempted to determine whether, on reaching the melting point, the elastic limit drops to zero or retains some small but definite value and reaches zero by a jump in the fluid state. Experiment was

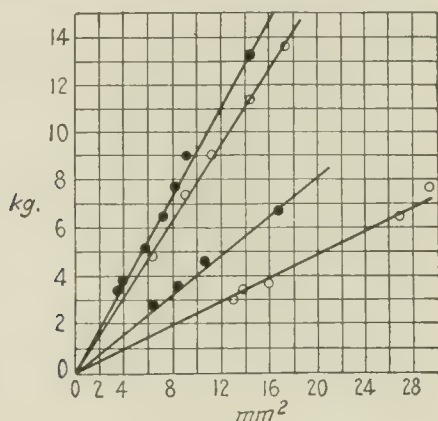


FIG. 16.

able to answer only this: that the jump is less than some measurable limit. We ascertained that this jump is less than one one-thousandth of the limit at room temperature. The load corresponding to the room temperature limit was about 3 kg. We therefore loaded the crystal by 3 g. and, steadily increasing the temperature, observed the change in the picture before the melting point was reached. The sharpness of the edges proved that we were below the melting point. Besides this proof, the beginning of melting is distinctly observable by the appearance of irregularly scattered X-rays and by a general illumination of the fluorescent screen.

The coincidence of the melting point with the point where the destruction limit becomes zero may be supposed to

have a physical significance, if we assume that the mechanism of fusion is equivalent to the same kind of destruction that is responsible for the limit at lower temperatures. When the slightest shear suffices to produce a destruction, the existence of a lattice becomes impossible and the heat absorbed by the crystal is applied to bring the atoms into a new form of equilibrium. Possibly this may explain why we do not know any example of superheated crystals while all other limits may as a rule be exceeded.

In a paper published last summer in *Zeitschrift für Physik* Georgieff found in bismuth a finite elastic limit at the

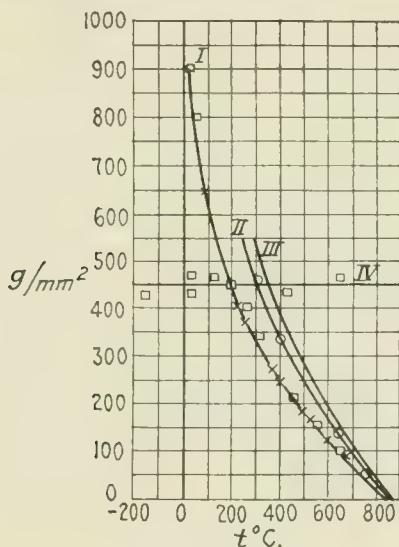


FIG. 17.

melting point. The shape of his curve, which seems first to drop to zero and change suddenly near to the melting point, makes it probable that his results were influenced by recrystallization. We are investigating the substance more closely.

The destruction limit depends upon the direction of the tensile stress in a crystal, which produces slips in the plane (110). The slip occurs in a definite crystallographic plane and, therefore, we would expect the slip to be related to the

shearing stress in this plane and not to the tensile stress. In fact, the destruction limit depends on the orientation of the tension. This is shown in Fig. 17, where the curve I corresponds to the direction (100) of the applied tension, the curve II was measured for the direction (110), and the curve III for (111).

It may be noticed that all curves reach zero at the same point—the melting point. The numerical value of the ratio of stresses for two directions however, does not correspond to equal shears in some (110) planes. The limit must, therefore, depend not only on the magnitude of the shearing stress in the (110) plane, but also upon the direction of sliding in this plane. This result is not surprising if we remember the structure of the (110) plane in a crystal like rock salt. In fact, gliding along the direction (110), a row of positive ions slides on negative ions somewhat like a train moving on rails. In moving in the direction (100) in the same plane the positive ions are alternately attracted by negative ions and repelled by the positive, so that the movement reminds one of a car going over hills and valleys. While this general conclusion was checked, still we have not succeeded in finding the dependence of the limit on the orientation in the plane (110) and in investigating the possibility of slips in planes other than the (110) plane.

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LECTURE V

THE MECHANISM OF PLASTIC DEFORMATION

The destruction limit, as measured by the *X*-ray method, gives the stress which produces an irreversible change in the structure of a crystal. The crystal becomes pulverized and the small fragments slip and turn in a quite irregular manner, while they continue to adhere to each other. The process of plasticity does not affect the transparency of the crystal; consequently there are no holes of the dimensions of a wave length of light or more produced in the destruction. Furthermore, the cohesion does not drop in value in a crystal so destroyed but, on the contrary, the rupture of a plastically deformed crystal requires a higher tension than for a single crystal. Thus, we must conclude that the separation involved in the plastic destruction does not exceed in magnitude the atomic distances. These conditions combined with the conditions for slip which is confined to one of the planes (110) only, and is limited to the direction of the shear, limit the irregularity of the arrangement of the fragments possible. The product of a plastic deformation after a compression or a tension is not like a compressed powder, but reminds one rather of a fibrous structure with a definite axis or a definite plane of symmetry. A complete recovery after such a destruction cannot be produced by an opposite deformation. The process involved in plasticity is irreversible, not only in the sense that the exerted work is transformed into heat, but also in the sense that, even by applying work in the opposite direction, we are unable to restore the initial state.

The evidence which we obtained for an internal destruction during a plastic deformation does not exclude the possibility of another kind of permanent set such as we have considered above for the bending of rock salt—defor-

mation consisting in a series of slippings parallel to some crystallographic axis without rotation. Such a deformation would not be revealed by X-rays, because there is no change in the orientation of the atomic planes reflecting the X-rays. This kind of deformation can, however, be observed by other methods, such as a precise measurement of the size and shape of the crystal or an investigation in polarized light.

Miss Levitsky measured the angle between the ends of a bent rod of rock salt, using the reflection from three mirrors fastened to the rod. She noticed carefully the first appearance of a permanent set and compared this with the load necessary to produce an irreversible change in the X-ray picture. These measurements showed that a preliminary stage of plastic deformation seems to exist in which the slip progresses in the manner shown in Fig. 14, without rotation. This kind of plastic deformation, while also irreversible and also producing heat, may be removed by a stress of the opposite sign.

Consequently we must distinguish two limits: (1) the elastic limit producing the first permanent set by slip of crystalline sheets parallel to some crystallographic direction without appreciable rotation; and (2) the destruction limit which is reached at higher stresses as manifested by a change in the X-ray pattern. This consists of a sliding in two or more planes, leading to a rotation of single fragments around some axis. If we imagine, for instance, in rock salt a gliding in two (110) planes under an angle of 45 deg. to the direction of tension, which is the direction (100), then we obtain a rotation around an axis (100), lying in both slip planes simultaneously. For many metallic crystals the planes of easy slip were investigated during the last three years, in order to account for the phenomena of the cold working of metals. These indicate that the described properties of rock salt are typical for all crystals.

A plastically deformed crystal is no longer a single crystal, but an aggregate of small crystals displaced and joined together to make a whole. One may ask whether

the lattice of a single fragment is affected by the plastic deformation. An investigation in polarized light shows strains in the crystals due to internal stresses between the grains. Those stresses, however, might be removed by an annealing of the crystal at a high temperature. The structure of the single fragments was then investigated by the Debye-Hull X-ray method, using monochromatic silver rays. This method shows the atomic distances to be independent of the orientation of the individual crystals. It was shown that, in spite of the extensive deformation of the whole crystal, the single grains remain unchanged.

The apparent contradiction before stated between the possibility of a plastic deformation and the idea of a crystal lattice, therefore, is now cleared up. No change in a crystal lattice has ever been observed without external forces equilibrizing the internal stress produced by the deformation of the lattice. A lattice, consequently, may be considered as an equilibrium state of atoms displaced by external forces only, in accordance with the model we are using. The fragments of a plastically deformed crystal are distinguished from the original crystal by their size only, contrary to the opinion of O. Lehmann, who thought it necessary to assume a new modification of the crystal subjected to a plastic deformation (homotropy of the second kind).

A very useful and powerful method for an investigation of a deformation in crystals is the observation of the crystal in polarized light between two Nicols. If the crystal is transparent and of a cubic system, it will not show double refraction unless under stress. The amount of the double refraction is proportional to the shearing stress or to the difference of the two principal stresses. While never yet so used, the optical method may be applied to measure the uniform pressure, giving the bulk modulus. Obreimoff and Sinelnicov developed a method of measuring the small changes in the refractive index produced by the change in density, by immersing the crystal in a liquid of the same refractive index. Definite mixtures are used

which permit an easy adjustment of the refractive index of the liquid. Combining both methods, we get the shear and the bulk deformation. This suffices for a complete description of the strain in an isotropic body, and in some crystals like rock salt.

An optical investigation of natural crystals has shown that they already have permanent internal stresses. A natural crystal is never dark between crossed Nicols. A prolonged annealing at 600 to 700°C. is necessary in order to remove the stresses and make the crystal really uniform. The construction of the apparatus used for the loading was carefully worked out in order to produce a uniform tension through the whole cross-section of the crystal. This was tested by the optical method itself. Gradually loading the crystal and observing the picture in polarized light, we observed the first appearance of a permanent set at stresses about one-tenth of those causing the destruction as observed by means of X-rays. A sharp bright line on a general dark background appeared and remained after removal of the load. At a constant load exceeding by a little the elastic limit, a second line parallel to the first one appeared after some time; then a third one and so on. All these lines represented projections of planes (110). More often they suddenly cross the whole crystal, sometimes beginning at one side and extending rapidly through the crystal to the opposite side.

On measuring the stresses in the crystal by compensation, it was shown that each such plane separates two parts of the crystal. The upper part is stretched, the lower one compressed. Both the tension and compression are greatest on the boundary and diminish with the distance from the slip plane. If we consider one strip of the crystal between two successive slip planes, we may notice that every strip is stretched in its lower layers and compressed in the upper layers. This means that all strips are under bending stress. In fact, after the process has progressed far enough and very thin strips are built, we may easily observe a curvature of the slip planes, going up

sometimes as high as to 30 deg. The distribution of the main stresses computed on the basis of the optical evidences is shown in Fig. 18a.

At a constant load the time interval between two successive slip movements increases steadily until no new slips are produced and a new elastic equilibrium at a stress exceeding the initial elastic limit is reached. We

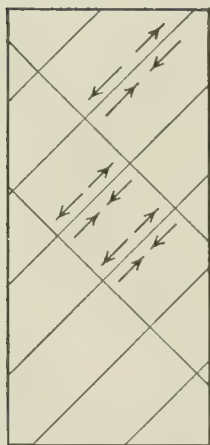


FIG. 18.

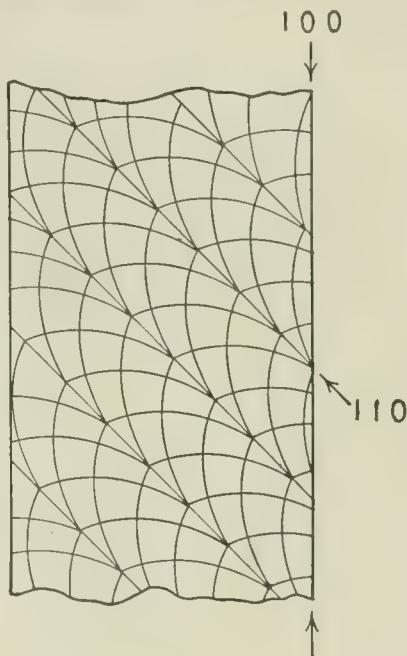


FIG. 18a.

must increase the load once more in order to see the process continued. The more slips already present, the higher the elastic limit which allows the appearance of supplementary slips. The distribution of the slip planes is quite uniform in any stage of the process. Each stage of the process might be characterized either by the number of slips present, by the curvature of the slip surfaces, or by the elastic limit. The general type of the picture described above is shown in Fig. 18.

The phenomenon of a plastic deformation of this sort consists in a series of slips parallel to some crystallographic plane and is produced by the shearing stress in this plane. For the sake of an adequate description of the phenomenon, it was desirable to study a pure uniform shear in its dependence of the orientation of the plane of slip, on the magnitude of the stress, and on the temperature. It may be expected that the slip will depend, even for the same plane (110) of easiest slip, upon the direction of the slip in this plane. In fact, a row of ions in the direction (100) lying in this plane consists of alternatively positive and negative ions. In the normal lattice every ion is opposed by an ion of the opposite sign in the next layer. Should the next layer slip against the first one in this direction, negative ions will, after a displacement by half an atomic distance, replace the positive ions. In this moment ions of equal sign will be opposed and consequently the layer that was first attracted will now be repelled. After the next half period, the attraction is restored and opposite ions meet once more. Thus the slip in the direction (100) will produce periodically attraction and repulsion of the sliding surfaces. The movement under such conditions must be similar to the motion of a car over bumps on a bad road.

Considering the direction (110) in the same plane (110) we find it consisting of ions of the same sign opposed by a row of opposite ions in the next layer. A sliding in this direction will progress under a steady attraction of the sliding surfaces. The magnitude only of the attraction will change, periodically. We may compare such a slip with a car moving on rails.

In Fig. 19 the distribution of ions in the plane (110) is shown and the directions (100) and (110) indicated. We must imagine the next layer above with the opposite charges over the lower atomic sheet. To exert a shear in a given direction, we clamped a rod of rock salt between two steel holders (Fig. 20). One of them, I, was fastened, the second, II, could move exactly parallel pushed by a

load P applied at a point over the slit between the holders I and II. By this arrangement a bending of the rod was suppressed to a minimum. The bending is proportional to the cube of the length while the shear is independent of the distance between two couples acting on the ends. The smaller the distance between the clamped ends, the smaller the bending. The stresses on the points indicated by the arrows S , however, soon exceed the elastic limit and a plastic deformation takes place resulting in an increase of bending. In reducing the cross-sectional area in the

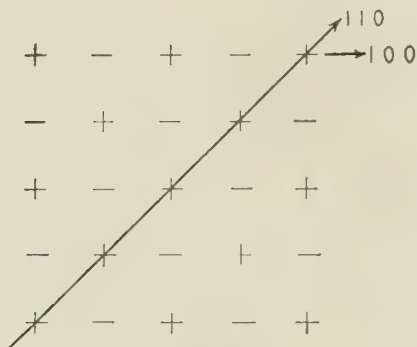


FIG. 19.

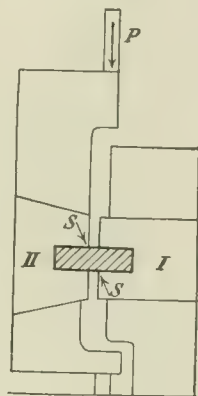


FIG. 20.

middle by an incision relative to the area clamped by the holders, we suppress this error to some extent.

While the quantitative investigation which is still in progress has not furnished definite results as yet, some qualitative results have been obtained which throw light on the phenomenon of plasticity. The investigation was first carried on by Prof. P. Ehrenfest and myself, and then continued by Miss Classen. We noticed that the shear of heated rock salt and zinc progresses by small jumps, each accompanied by a noise like a tick of a clock. In a quiet room those ticks are rather loud and follow at regular time intervals. Many hundreds of ticks may be noticed, their frequency depending upon the load applied.

Miss Classen measured the relative displacement of the holders by the reflection from two mirrors using an enlargement of ten thousand fold. She found that not only are the time intervals between two jumps remarkably constant, but the magnitude of the single jumps remain constant, within 10 per cent under given conditions. Thousands of jumps could be observed. The time intervals increase, however, gradually until the jumps become rare and finally cease. The magnitude of a jump remains constant. Figure 21 gives a general idea of the progress of the deformation with the time. Increasing

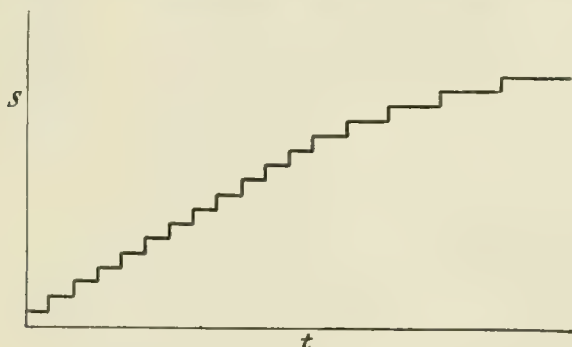


FIG. 21.

the load P , we increase the frequency Z of the jumps. As the frequency is zero at the elastic limit P_0 , we may consider the frequency as some function of $(P - P_0)$. The magnitude of a jump S seems to be independent of $(P - P_0)$ both if P changes or P_0 increases. For small values of $(P - P_0)$ the time interval between two jumps may be as large as 30 min., while the regularity of the phenomenon remains unchanged.

At lower temperatures the magnitude of the jumps decreases. We may assume S to be a function of temperature.

As pointed out above, the elastic limit P_0 increases with the number N of slips already produced in a unit of length L .

According to this statement, we may set

$$Z = \frac{\Delta N}{\Delta t} = F(P - P_o), \quad (28)$$

$$P_o = f\left(\frac{N}{L}\right), \quad (29)$$

$$S = \varphi(T). \quad (30)$$

The velocity of the plastic deformation S may be expressed by:

$$V_p = \frac{\Delta S}{\Delta t} = ZS = \phi(P, N)\varphi(T). \quad (31)$$

This velocity differs in principle from the similar velocity V_f of a viscous liquid. The momentum ΔG , transferred through unit area during the time Δt in a viscous liquid where the velocity of two sheets at a distance Δx differs by Δv , will be:

$$\Delta G = \eta \frac{\Delta v}{\Delta x} \Delta t$$

if η is the coefficient of the internal friction. The frictional force P per unit area is then equal to:

$$P = \eta \frac{\Delta v}{\Delta x}.$$

If the velocity of one sheet is zero, and that of the other v_f , then

$$P = \eta \frac{v_f}{\Delta x},$$

or

$$v_f = \frac{1}{\eta} P \Delta x. \quad (32)$$

The resistance to a flow is due to a transfer of momentum and is produced by a gradient of velocities in the direction x . Nothing analogous may be found for the plastic deformation, in spite of the similarity of the mathematical laws. The plastic deformation progresses by jumps. In the time interval between two jumps the velocities are zero throughout the whole crystal. During the jump they are independent of the acting force. The force determines the number of jumps per second or the time interval

between two successive jumps. The force influences some process going on during this time which prepares for the next jump. This process is now the most important problem in the explanation of a plastic deformation. A second problem involves the explanation of the constancy of S . Finally, we must explain why the distribution of the slip planes $\Delta N/\Delta L$ is so uniform. Neither Z , S , or even $\Delta N/\Delta L$ show a statistical character. Contrary to what we would expect, they are determined by precise laws, in which the deviations do not exceed the experimental errors.

Our knowledge about the mechanism of a plastic deformation and the quantitative laws governing it is insufficient to propose a definite theory. Nevertheless, we will enumerate the possible hypotheses, explaining the mysterious facts described above.

The increase of the elastic limit by a plastic deformation, or using the language of mechanical engineers, by cold working, is now often ascribed to a bending of the crystal-line strips. It is assumed that gliding is easier in a normal crystal with plane surfaces than in a crystal with curved atomic surfaces, as actually observed after a plastic deformation. While the curvature really exists it is difficult to see how this fact may account for the problem, for a gliding along a smooth curved plane should be almost as easy as along a flat one.

Another hypothesis that suggests itself assumes that the slip in some plane destroys the regularity of the atomic structure. The surface becomes rough on an atomic scale. This irregularity extends from the slip plane in the interior of the crystal and diminishes gradually with the distance. The more irregular a given part of a crystal is, the higher must be the force to produce a gliding. It is then easily seen that a new slip will occur in the middle of a strip where the distortion is least, and first in the largest strip. The elastic limit depends upon the distance of the new slip plane from the next slip surface. Both the increase of the elastic limit with the number of slips per unit length, and the distribution of the slip planes at equal relative

distances are explained by this hypothesis. Heat agitation will gradually destroy the irregularities and make the next jump possible after the lapse of some time.

A third hypothesis might consider the slip as a discharge of the elastic energy stored up in a single strip. A slip results in two new surfaces with a destroyed lattice. Such surfaces will have higher potential energy than the initial crystal. If the slip takes place in a time shorter than would be necessary for a sound to travel through the whole crystal, the energy must be furnished by a small part of the crystal in the neighborhood of the new surface. The previous slips represent sheets with a different sound velocity that will reflect the elastic waves going to the plane where a new slip occurs. It is therefore possible that the energy will be taken from one or a few strips only. The supply of the energy U in a strip of the thickness D and the surface S at a stress p will be

$$U_1 = \frac{1}{2}ED \cdot S \cdot p^2,$$

and the energy necessary for a slip

$$U_2 = 2\alpha S.$$

The lowest stress p_0 producing a new slip, that is, the elastic limit, is

$$p_0 = 2\sqrt{\frac{\alpha}{E}} \cdot \sqrt{\frac{1}{D}} \quad (33)$$

Equation (33) would explain the uniformity of strips and the increase of the elastic limit by the cold working. Considering the conditions after a slip as a new kind of an elastic equilibrium corresponding to an amorphous state, we might find some explanation for the constancy of the magnitude of a slip.

Unless more accurate data are obtained and the form of the equations (28), (29), and (30) are disclosed by new experiments, a further discussion of the mechanism of a plastic deformation seems to be useless. We may state, however, that while the model of a crystal lattice in its actual form was shown to be insufficient for the explanation of the plastic deformation, no evidence was found against the fundamental assumptions of our model in this domain,

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LECTURE VI

STRENGTH

The most striking contradictions with the predictions of the electric theory of crystal lattices are met when we consider the strength of solids. We have computed the maximum cohesive force in rock salt resulting from the electrical theory of crystal lattices and found it to be of the order of magnitude of 300 kg. per mm.² for a uniform tensile stress. A unidimensional tension would, at room temperature, give about 200 kg. per mm.² The observed tensile strength of single crystals of rock salt does not, however, exceed 0.5 kg. per mm.² When we took care to exert a tension uniformly distributed over the cross-section and to avoid the eccentric forces which produce bending, the single values obtained were spread over an interval of no more than 10 per cent of the observed value, the average strength being 0.44 kg. per mm.² A lowering of temperature to the temperature of liquid air does not appreciably change the strength of rock salt. Neither was a change found by heating up to 200°C. (curve IV in Fig. 17). Beyond this temperature the strength seemed to increase.

It was, however, found that at these temperatures the strength was not measured on single crystals, but on crystal aggregates. This was explained by the fact that at 200°C. the destruction limit drops to a value 0.44 kg. per mm.², which is equal to the tensile strength. Thus, at temperatures higher than 200°C. the elastic limit is lower than the strength. Increasing the load gradually we first reach the elastic limit and a plastic deformation takes place which destroys the lattice of the crystal. As has been already stated, the process of a plastic deformation increases the strength many times.

In order to formulate some quantitative law for the dependence of the strength upon the degree of the deformation and of the distortion of the lattice, we determined this degree by the change produced in the cross-section. We have seen that the plastic stretching of a crystal consists of a slipping along some crystallographic plane, the (110) plane for rock salt. As a result of such a slipping (Fig. 22), a cylindrical rod changes to a band of a breadth B equal to the initial diameter of the rod and a thickness D which gradually decreases as the stretching progresses. The cross-section s becomes smaller than the initial area S . The ratio S/s furnishes a fairly good measure of the progression of the plastic deformation. Plotting the strength against this ratio, we found a relation given in Fig. 23. At a deformation measured by $S/s = 35$, the strength reached 5 kg. per mm.², about twelve times the strength of a single crystal.



FIG. 22.

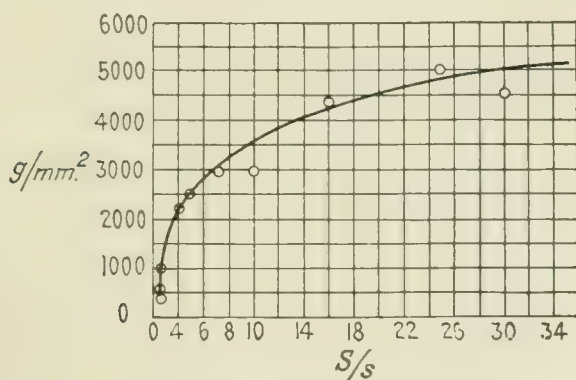


FIG. 23.

above 200°C., but corresponds to the strength for the degree of a plastic deformation reached at the moment when the crystal was broken. As plastic deformation takes time

to develop, however, we may expect that by shortening the time interval between the exceeding of the elastic limit and the final rupture, we will decrease the error. In fact, by shortening this time we were able to observe a much lower strength, up to $650^{\circ}\text{C}.$, than originally measured. This reached some constant lower limit. Sharp shocks in loading, however, must be avoided to obtain this result. We must then consider this constant lower limit as the strength of the single crystal. Its value was of the same magnitude up to $600^{\circ}\text{C}.$ as at room temperature, as indicated in Fig. 17. Thus in the range of temperatures between $-180^{\circ}\text{C}.$ and $+650^{\circ}\text{C}.$ the strength of rock salt is approximately constant.

The crossing of the curves representing the strength with the curves representing the elastic limit seems to be a general property of all crystals. Thus the strength exceeds the elastic limit on approaching the melting point, where the elastic limit drops to zero. At sufficiently low temperatures the elastic limit increases faster than the strength and exceeds the strength. At the higher temperatures the rupture of the crystal will be that of a plastic body; in the lower temperature range it will be that of a brittle one; *i.e.*, rupture occurs before any plastic deformation takes place. Consequently, the brittleness and the plasticity are not properties of different bodies, but both are determined by the temperature and the degree of deformation of the same body. Every body is brittle at low temperatures and plastic at high temperatures. The intersection in Fig. 17 for a given kind of deformation determines the temperature at which a brittle body becomes flexible. We do not need, as O. Lehmann has done, to assume a special homotropy of the second kind in rock salt to explain the plasticity which exists at high temperatures, but which does not exist at low temperatures.

A proper choice of temperature may give to the substance just the desirable mechanical properties. For instance, when machining single crystals such as lead or zinc, we may avoid a plastic deformation and a deterioration of the

crystals by lowering the temperature with liquid air. In other cases, a heating is advisable.

The tensile strength of single crystals is about five hundred times less than the calculated maximum for the cohesive forces and rupture occurs before an essential deviation from Hooke's law can be noticed. Even the strength of plastically deformed crystals is forty times less than we should expect. If the electric theory is not wrong in its fundamental assumptions, such a discrepancy should not exist. It is possible, however, that the usual phenomenon of rupture by tension has nothing to do with the true cohesive force. We can easily see that a *tearing* rupture would require a much lower force than a simultaneous rupture across the whole cross-section. Assume, for instance, that a small but a very sharp crevice exists on the side surface of a stretched rod. The stress distribution will show a high concentration of stress at the edge of the crevice as indicated in the diagram given in Fig. 24. The ratio of the stress at the edge to the average stress over the



FIG. 24.

cross-section may be very high if the radius of curvature of the end of the crevice is small enough, a thing which might be expected to exist in a crystal. In fact, a ratio of stress at the crevice to average stress over the cross-section reaching many hundreds would not be surprising. Comparing the energy in this state with the energy which would be produced when the crevice increases, Griffith and Wolf formulated the conditions for a progressing crevice, which means a tear ending in a final rupture of the body. Griffith succeeded in showing experimentally how far depressed the strength may be by such crevices.

If this were the explanation of the weakness of crystals under tension, we might expect a perceptible influence to be exerted by the surface where the tear and rupture start and we must find an explanation for the fact that the tensile strength has a constant value within 10 per cent.

An influence of the surface upon the strength of rock salt was actually observed and described by W. Voigt and Sella, and by H. Müller.

The first authors found that the tensile strength of rock-salt crystals depends not only on the orientation of the stress, but on the orientation of the external surfaces bounding the crystal. They found, for instance, that the strength for a crystal with (110) surfaces was almost twice that for a crystal with (100) surfaces. It must be remembered, however, from our point of view that the sharpness of edges of the crystal is quite different in the two cases. I tried to avoid this objection by preparing crystals where the actual surface was different for the same shape of the crystal and the edges were always rounded, as indicated in Fig. 25, showing the cross-section of several rods of rock salt. No essential influence of the order of magnitude given by Voigt and Sella, however, was noticed on these samples. The values of the tensile strength in these experiments were spread over a larger interval than usual.

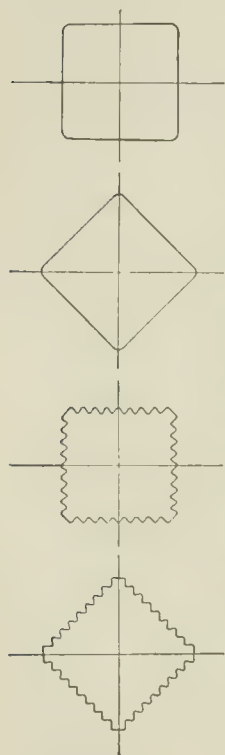


FIG. 25.

H. Müller found that the strength defined by the tensile stress per unit of cross-section increases from 0.5 kg. per mm^2 to about 7 kg. per mm^2 , when the cross-section decreases from about 20 mm^2 to 0.3 mm^2 . This would indicate

that the strength depends not only upon the cross-section but also upon the perimeter. Contrary to this statement, Miss Levitzky was unable to find any influence of the perimeter between the limits of 36 and 0.1 mm^2 for the cross-section, when uniformly prepared crystals were used. We suspect that the results of H. Müller are due to a treatment of the crystals by water, which will be shown

to greatly influence the strength. In Fig. 26, curve I indicates the results of Müller, and curve II, the measurements of Miss Levitsky. While no influence was found for pieces of a thickness down to 0.1 mm. for very thin crystals of mica, an increase of strength about four times was found by A. Walther, between 0.01 and 0.001 mm. of thickness; and this influence was still twice as great at liquid air temperatures.

Neither the experiments of Voigt and Sella nor those of H. Müller establish the importance of the surface condi-

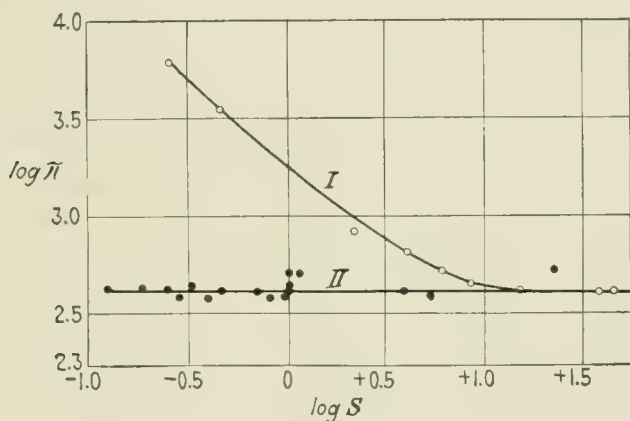


FIG. 26.

tions for the rupture of rock salt of ordinary dimensions. If the surface crevices are really responsible for the rupture of crystals, they must be produced by some regular process and their depth and sharpness must be given by the crystal structure. The increase of the strength at thicknesses of the order of magnitude of 1μ indicates that the crevices may have dimensions of about 0.1μ to 0.01μ , or 10^{-5} to 10^{-6} cm.

While the experiments described do not check the surface theory of the strength, they are not contradictory to this hypothesis. We may suppose, however, that whatever the mechanism of the appearance of crevices may be, it

takes some time to produce them. Thus, a fresh surface will be different from an old surface. Continually renewing the surface by dissolving in water, we may prevent the crevices. The faster the old surface is removed by water, the more probable it is that crevices will not have time to be produced. Some indications of this kind were present in the property exhibited by rock salt of becoming plastic in water, which means that the strength exceeds the elastic limit.

Miss Levitsky and I, therefore, tried to rupture rock-salt crystals which were immersed in hot water and found that the strength increased considerably. In fact, the rock salt always broke at a dry section, even when the dry cross-section was as much as ten times greater than that under water. Dissolving continuously, we reduced the wet section until the crystal broke at a very thin place of about 0.2 mm. thickness, while the dry section was about 6 mm. thick. Computing the stress at the rupture as the ratio of the applied load to the cross-section, we got strengths up to 30 and even 160 kg. per mm.², which approaches the theoretical strength of 200 kg. per mm.² as closely as one could expect.

Before the rupture occurred, the destruction limit was reached, as it corresponds to 0.9 kg. per mm.² at room temperature, and the crystal was in the state of a plastic deformation when rupture occurred. The measured strength was, therefore, not the strength of a single crystal, but of a crystal aggregate. Nevertheless, the result is important for the electric theory of crystals, because it shows that the internal cohesion of rock salt is not less than 160 kg. per mm.² and that rock-salt crystals, even small ones, can stand such stresses. This result confirms the calculation of the cohesive forces given by the theory in a satisfactory manner.

M. Polanyi and W. Ewald objected to our results. They expressed the opinion that the influence of water consists in a decrease of the elastic limit and not in an increase of the strength. Thus, rock salt would become plastic and

its strength would increase by the process of the plastic deformation as shown before and given in Fig. 23. While this reasoning might be correct, the actual process does not correspond to this statement. We have measured both the destruction limit as indicated by X-rays, and the strength of a single crystal as given by a rapidly increasing force. Contrary to the assumptions of Polanyi and W. Ewald, we found that the destruction limit was within 1 per cent the same both in water and in dry air. The strength was found to be at least ten times higher while the crystal was in water. If, however, the crystal was not broken in water by the high stress of 5 kg. per mm.², it showed, on being dried, the normal small strength of 0.4 kg. per mm.² corresponding to an undeformed crystal. This direct test of Polanyi and Ewald's hypothesis has not confirmed it, but on the contrary, proved the increase of strength in water to be independent of plastic deformation.

It is of interest to determine what time is actually necessary in order to bring a fresh surface with a high strength to the normal conditions in which it is supposed to contain small crevices. This is best seen in testing rock salt under a bending stress. At room temperature the elastic limit for bending seems to be a little below the breaking stress. Dry pieces of rock salt are brittle under bending stresses. Under water they become flexible, which is an indication of the increase of the strength. If we remove the samples from water it is found that some of them remain flexible over a period of many seconds, minutes, and a few of them even for days, especially if put into a vacuum. Samples of different origin behave differently. Some become brittle immediately after removal from water.

It must be stated in passing that a saturated solution of salt or a dry oil did not influence the strength. This was also found to be true for gases such as hydrogen, carbon dioxide, and for a conservation during many days in vacuum. The strength was always about 0.5 kg. per mm.².

While the rupture of rock salt in hot water actually gave the expected strength, it was not the strength of a single crystal. Experimental difficulties did not permit us to measure in water stresses more than 10 kg. per mm.² on single crystals.

There is another way of avoiding the influence of surface crevices. If the distribution of stresses is such that the surface layers are not under tension, the influence of the surface will be excluded. Neither crevices nor any other phenomenon on the surface can influence the process of rupture going on inside where the stress reaches its maximum value. One may realize a test of this sort if we suddenly and uniformly heat a sphere. The outside layers will expand first and stretch the central cold part of the sphere, exerting a uniform tension. This is just the kind of deformation which was used in order to compute the cohesive forces from the electrical theory of crystal lattices. It is clear that there cannot exist a radial tension in the surface layer at any time because the surface is free to expand and no forces are acting on the surface. The distribution of stresses inside the sphere was computed by G. Grünberg. It consisted of a uniform tension T , progressing from the surface to the center and reaching there after a time τ determined by the heat conductivity. It has a maximum value given by:

$$T_{\max} = A(t - t_0),$$

where A is a coefficient equal to 0.08 kg. per mm.² for rock salt and t and t_0 denote the initial and final temperatures of the sphere.

The time τ was shown for rock salt to be equal to

$$\tau = 1.9 \cdot r^2,$$

where r is the radius of the sphere.

Beside the radial tension, there was also found to be a tangential stress, which would result in a compression which would not be zero at the surface during the initial stages of heating. The compression is, however, not as serious in its effect on the strength as tension is.

Several spheres of rock salt were cooled in liquid air and then plunged suddenly into hot water at $+100^{\circ}\text{C}$. and fused lead at $+600^{\circ}\text{C}$. There was no cracking or rupture if precautions were taken to produce a uniform heating of the sphere. The maximum uniform tension at the center in these experiments must have been as high as 60 kg. per mm.² The central part was cold so that the crystal lattice was not destroyed. A plastic deformation of external layers may have been present, but the amount of deformation during the half-second necessary to produce the stress of 60 kg. per mm.² in the center could not be large. In fact, no traces of this deformation were observed on small spheres. We may be sure, therefore, that the actual tension in the center was not essentially less than the value computed on the assumption of a complete elasticity.

While the sphere experiment did not furnish a quantitative value of the true cohesive strength, it proved that this cohesion is higher than 60 kg. per mm.² It thus proved that the small strength of solids usually measured has nothing to do with the true cohesion. The latter is of the order of magnitude predicted by the theory.

The problems of the tensile strength of solids, the influence of the size and arrangement of crystalline grains, of cold working, and so on, involve, presumably, the process of growth of small crystalline crevices throughout the grains and on boundaries of the grains. The electrically computed theoretical cohesive strength thus gives us the upper limit for the strength of the crystal, which is the highest that can be achieved.

The investigation of the elastic properties of crystals in this and the preceding lectures led us to the conclusion that the observed facts are, without exception, consistent with the electrical theory of crystal lattices. All apparent contradictions seemingly introduced by the elastic after-effect, the plasticity, and strength, were shown to be in reality no contradictions at all. The general predictions of the theory were checked both qualitatively and quantitatively. It was found, however, that the actual form of

the theory does not suffice to account for the mechanism of some of the elastic phenomena such as slipping in the crystal lattice, the crevices on the surface, etc. A detailed study of these phenomena is needed in order to complete our model of a crystal.

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LECTURE VII

CONDUCTION OF ELECTRICITY THROUGH CRYSTALS

The behavior of a dielectric in an electric field leads us to ascribe to it, besides a dielectric polarization, the property of conducting electric charges. Both phenomena, the polarization and the conductivity, are, however, so closely related in their manifestations that they often cannot be distinguished. Thus, the whole problem has been denoted as a kind of dielectric anomaly. Maxwell pointed out that a heterogeneous dielectric consisting of alternating sheets with different ratios of the specific conductivity to the dielectric constant would in an electric field produce phenomena of this kind, known under the name of the electric aftermath or residual charge. Muraoka checked Maxwell's prediction experimentally.

We have seen that an analogous *elastic* after-effect disappeared when a pure and single crystal was investigated. The laws governing both the elastic and electric after-effects are so similar that we might suspect a similar mechanism to produce both. The suspicion that single crystals will be free from after-effects was, however, bound to be wrong. Nevertheless, by using single homogeneous crystals, we are sure of avoiding at least the phenomenon due to an after-effect of the Maxwellian type. We may hope, therefore, that the explanation of the remaining phenomena will be easier. Thus, a study of the electric properties of solid dielectrics has to begin with an investigation of single crystals.

The most detailed investigation of different natural crystals was published in 1888 by Jacques and Pierre Curie. This beautiful work established the standard method of measurement which was also employed in our work, and the fundamental properties of crystals.

A plate K cut out of a crystal in a given crystallographic orientation was provided with two metallic electrodes (Fig. 27). One of them, M , could be charged to a constant high potential. The second, L , could be connected to an electrometer E (usually a string electrometer) which may be either earthed or isolated for a given time τ . Denoting the potential indicated by the electrometer after this time by V , and the total capacity of the electrometer, plate and connections by C , we may define the current I going through the plate by

$$I = \frac{V \cdot C}{\tau}. \quad (1)$$

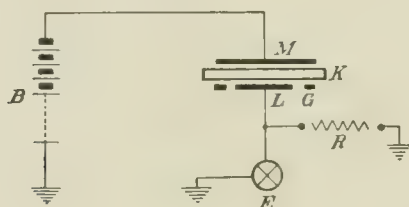


FIG. 27.

For measuring larger currents we used a resistance R introduced between the electrode L and the earth. The current is given in this case by

$$I = \frac{V}{R}.$$

In order to prevent a charging of the electrometer by a current flowing over the surface of the plate, the isolated electrode L was surrounded by an earthed guard ring G .

At the instant when the electrode M is charged, a charge $Q_o = CV$ appears on the electrode L , due to the dielectric polarization. From this Q_o the dielectric constant ϵ may be computed by the relation

$$\epsilon = \frac{4\pi Q_o d}{S \cdot V_o} = \frac{4\pi C d}{S} \cdot \frac{V_c}{V_o}, \quad (2)$$

where d denotes the thickness of the plate, S the area of the electrode L , V_o the applied potential, and V_c the induced potential at the electrometer. The electrometer

is next momentarily earthed and then again isolated after which further charges appear which are now to be ascribed to the conductivity σ , defined by

$$\sigma = \frac{Id}{SV_o} = \frac{Cd}{S} \left(\frac{V}{V_o\tau} \right) \quad (3)$$

where I corresponds to equation (1).

Combining equations (2) and (3), we find:

$$\frac{\sigma}{\epsilon} = \frac{1}{4\pi} \frac{V}{V_o\tau} \quad (4)$$

If the dielectric constant is known or once measured, we may thus avoid the determination of the geometric dimensions S and d and of the capacity C , by using equation (4).

The current I as defined by equation (1) is, however, not a constant; and thus the conductivity defined as in equation (3) is also not a constant. The current diminishes steadily, at first rapidly and then more slowly, but continuously during many days. The question then arises as to what value of the current to use in representing the conductivity. Curie chose the current flowing 1 min. after the potential V_o had been applied. F. Braun suggested that one use the current after 24 hours, when the decrease becomes inappreciable during a time interval such as a few hours. Both definitions differ many tens or hundreds of times. It is obvious that no reasonable choice may be made without knowledge of the cause producing the decrease of the current. We must, therefore, first find the explanation.

The phenomenon, as pointed out by Curie and many other investigators, may be described as follows: Applying a constant potential to a crystalline plate, we get a current I diminishing steadily. A final value, if ever, will be reached asymptotically after a very long time to be measured sometimes in minutes, sometimes in hours, and sometimes even in days and months. This final current I_f is often but a small fraction of the initial current I_o , sometimes being as small as 10^{-4} of it. When the potential V_o is removed and both electrodes M and L are connected

at some time T , an opposite current $-I_p$ appears. This decreases steadily and reaches zero asymptotically after a time of the same order of magnitude as the primary current I , as shown on Fig. 28.

The current I_p may be represented as a difference of a current $-I$, plotted from the moment T and falling off at the same rate as $+I$ and the primary positive current extrapolated for $t > T$. This law of superposition holds for any change in the applied potential ΔV .

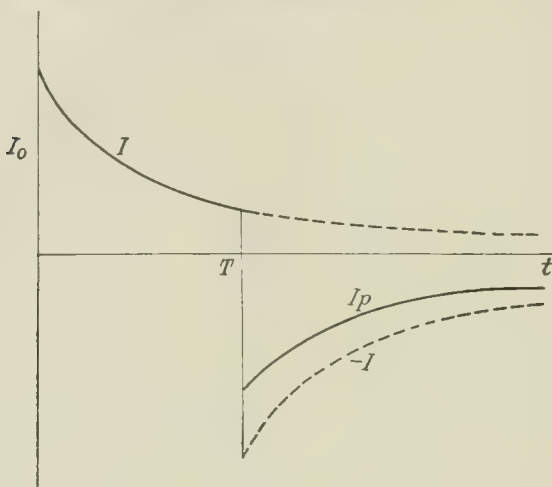


FIG. 28.

Let us represent the primary current ΔI_t produced by a potential difference ΔV at some time t by:

$$\Delta I = g\Delta V = g_0\Delta V\varphi(t), \quad (5)$$

where $\varphi(t)$ denotes the decrease of a unit initial current at the time t , and g_0 the initial conductance of the plate, given by

$$g = \frac{1}{R} = \sigma_d', \quad (6)$$

where R denotes the resistance of the plate.

For a potential ΔV_T applied at the time T , the current at the later time t will be:

$$\Delta I_t = g_0\Delta V_T\varphi(t - T).$$

The current I produced by all changes of potential applied to the plate from $t = 0$ till $t > T$ may be set equal to

$$I = \Sigma \Delta I_t = g_0 \sum_{T=0}^{T=t} \Delta V_T \varphi(t - T). \quad (7)$$

For a continuously changing potential we get:

$$I = g_0 \int_0^t \frac{\partial V}{\partial T} \varphi(t - T) dT. \quad (8)$$

Equations (7) and (8), representing the law of superposition, were checked for many dielectrics at room temperature. They are not applicable, however to all dielectrics without exception.

Several theories were proposed to give account of the phenomena described. In spite of their faultiness we shall enumerate some of them because they fix attention on different important phases of the problem to be discussed. This will be useful for the formulation of the final explanation resulting from our investigations.

1. Assuming that the superposition law holds strictly, we notice that, properly speaking, there is no current flowing through the crystal, because connecting the electrodes we get back the same charge $Q = \int_T^\infty I dt$ in the inverse current $-I_p$ as was engaged in the direct current I . In fact, the current I flowing from $t = 0$ till $t = T$ transferred the charge Q_1 ,

$$Q_1 = \int_0^T I_t dt,$$

and the inverse current a charge Q_2 ,

$$Q_2 = \int_T^\infty I_p dt.$$

The superposition law assumes, however, that

$$I_p = I_{t-T} - I_t,$$

and therefore

$$Q_2 = \int_T^\infty I_{t-T} dt - \int_T^\infty I_t dt.$$

We substitute in the first term $t - T = \tau$ and get then

$$Q_2 = \int_0^\infty I_\tau d\tau - \int_T^\infty I_t dt = \int_0^T I_t dt = Q_1.$$

It would be shown in a similar way, that for any function $V = f(t)$ around a closed path such that the initial and the final value of V are zero, the total charge

$$Q = \oint I dt = 0. \quad (9)$$

Emphasizing this property, we may be inclined to deny the existence of any current in the dielectric and to ascribe the temporarily appearing charges to some anomalies of the dielectric polarization. Assuming that the dielectric constant increases in an electric field gradually from some initial value ϵ_o to ϵ_f , the induced charge Q_o will then increase to Q_f . The corresponding current at some instant t is given by

$$I_t = \frac{dQ}{dt} = V_o \frac{S}{4\pi d} \frac{d\epsilon}{dt}, \quad (10)$$

and the total charge of the electrometer produced by the direct current is

$$Q = Q_f - Q_o = \int_0^\infty I_t dt = V_o \frac{S}{4\pi d} (\epsilon_f - \epsilon_o).$$

In some cases, $Q_f - Q_o$ is only a fraction of Q_o , and the explanation then seems to be reasonable. We may assume, for instance, that besides the polarization proceeding with the velocity of light through the dielectric, a displacement of charges or a change of the orientation takes place gradually against a viscous resistance. It is probable that, for some viscous fluids containing dipolar molecules, such an explanation may hold. But it is wrong as a general theory of the phenomena, because $Q_f - Q_o$ is in most cases many hundred times higher than Q_o and could be made as high as desirable by increasing the temperature, so that the final value of ϵ will exceed any reasonable limit. In a pure solid crystal, we excluded the possibility of viscous processes from the picture which we are using as a model of a crystal, and we shall later see that no real signs of a change of the dielectric constant with the time have ever been observed. This theory is, therefore, untenable.

2. A second explanation denies the existence of a decrease of the current for a *pure crystal* and makes the irregularities

occurring in the usual solid dielectrics responsible for the phenomenon. Nicols observed, in fact, a much smaller electric after-effect in transparent crystals of calcite than in glass. This effect is, however, mainly a question of the time scale, as has since been shown. If the conductivity is small, the decrease of the current is slow and many days are necessary in order to observe the whole curve (Fig. 31). For a short time interval the curve may be approximated by a horizontal line. Increasing the temperature (or *dissolving some electrolytes* in the crystal) we may increase the conductivity and reduce the phenomenon to an entirely different time scale. We could observe, for instance, at 70°C. in half an hour the same effect that requires 10 days at 20°C. At 120°C. the same change will be produced during $\frac{1}{10}$ sec. The phenomenon described above cannot be explained by the heterogeneous structure of dielectrics. It may be observed as well in homogeneous single crystals such as calcite, quartz, rock salt, sodium nitrate, and the like.

3. A third explanation emphasizes the influence of chemical impurities, making these the determining factor. Hertz has observed in benzene a decrease of the conductivity due to a purification produced by the current itself. It is true that impurities are generally dissociated and that the current removes most of the ions of the impurities. Small colloidal particles often present in liquids also are charged and are thus transferred to the electrodes. By removing the ions and the particles, the current decreases the conductivity. On this theory then, the opposite current must be ascribed to a concentration cell produced by the preceding current. Many objections, however, may be raised against the primary importance of impurities for the theory of dielectrics.

The magnitude of the electromotive force of polarization which is given by the equation,

$$e = \frac{U_1 - U_2}{U_1 + U_2} \frac{RT}{F} \ln \frac{n_1}{n_2}, \quad (11)$$

will be far too small to explain the negative current I_p ,

especially if we take into account the diffusion which is proportional to the conductivity.

Explaining the decrease of the current by the removal of impurities, we must remember that the quantities of impurities transferred by the current according to Faraday's law are often many millions of times less than the quantities actually present. The theory fails to explain the phenomena quantitatively.

The superposition law requires a constancy in the properties of the dielectric during the whole process because each change in potential ΔV produces, according to this law, the same change of the current ΔI . A purification theory would require, on the contrary, that the current ΔI diminish gradually when equal potential changes ΔV are applied at different stages of purification.

While such phenomena as purification and cataphoresis are very important for many liquid dielectrics and must be seriously considered in solids, they are unable to explain the essential features of the electrical condition in crystals.

4. We might expect to approach an explanation if we could find the cause of the opposite current I_p . Warburg often found that using a direct current of $V_o = 600$ volts potential, he could not stop the negative flow of the current I_p by connecting in series a battery of 300 volts. Therefore, if the opposite current is due to some electromotive force, it must be higher than 300 volts. This cannot possibly be an electromotive force of an electrolytic polarization. Warburg gave up any attempt to explain it and contented himself with calling it merely "a polarization of a peculiar kind." Curie proposed a hypothesis explaining the magnitude of this electromotive force. He assumed that a crystal represents a storage battery of small cells with an electromotive force not exceeding a few volts, each connected in series by means of water distributed in some way inside the crystal. This battery is charged by the direct current and discharged by the opposite one. This hypothesis was supported by observations of the influence of a temporary heating to high temperatures upon

the conductivity at low temperatures. He ascribed the observed decrease of the conductivity after a heating to a removal of the absorbed water.

The investigation described below will show that such cells, which are not in accord with the model of a crystal which we are using, do not exist and that both the dependence of the current upon the time and the influence of heating have other origins than those assumed by Curie.

In 1904, in collaboration with Röntgen in Munich, I began the investigation of these phenomena and continued them at St. Petersburg in collaboration with Mrs. M. Kirpichewa. Both these collaborators died in 1923, and since then I have continued these researches.

The first step was to determine if, in spite of the apparently contrary results expressed by equations (5) and (6), a dielectric crystal may be characterized by some *definite specific conductivity*. The specific conductivity is defined by Ohm's law as the ratio of the density of the current to the electric field. Equation (1) may be identified with the conduction current if we exclude the displacement current produced by the change in the potential or the capacity. The field may be represented by the applied potential V_0 only in the case of a uniform field. The opposite current I_p appearing in the absence of an external potential V_0 shows, however, that the field cannot be due to the potential V_0 only. There must be some supplementary electromotive force P produced by the current. We tried, therefore, to measure this hypothetical force P by means of an electrometer of a small capacity. If one of the electrodes be connected to earth and the second to the isolated electrometer, the latter will be charged to a potential P_1 equal to the electromotive force existing at this moment at the plate. The charge taken by the electrometer due to the time elapsing during this measurement will produce small errors. Both errors may be reduced to a minimum, if we charge the electrometer with the isolated electrode previously for a moment to almost the expected potential and notice whether the potential

used was too high or too low. Instead of the process described, we used a strictly zero method which consisted of holding one electrode with the electrometer earthed, charging the opposite electrode for a moment to the expected potential, and then noticing in what direction the electrometer was charged. If the applied potential is accurately equal to P , there will be no current on making the contact. A small systematic error is introduced by the fact that P diminishes with the time, producing a displacement current. The corresponding change in the potential of the electrometer during a time interval Δt is

$$\Delta V_1 = \frac{C_p}{C_p + C_o} \frac{dP}{dt} \Delta t,$$

where C_o represents the capacity of the electrometer and the connections, and C_p that of the plate.

If the applied potential is not accurately equal to P , but differs from P by an amount ΔP , there will also be a conduction current. The potential difference thus produced at the electrometer in the same time Δt will be according to equation (4),

$$\Delta V_2 = \frac{4\pi C_p}{C_p + C_o} \frac{\sigma}{\epsilon} \Delta P \Delta t.$$

We obtain a zero current at first if $\Delta V_1 = \Delta V_2$. The error ΔP introduced by this cause is:

$$\Delta P = \frac{\epsilon}{4\pi\sigma} \frac{dP}{dt}. \quad (12)$$

The derivative dP/dt could be observed and a corresponding correction made. It is negligible, however, in most cases and the precaution need not be taken.

Using this method with the proper precautions, we ascertained that at all temperatures the magnitude of P could be measured and that by applying Ohm's law in the proper form,

$$I = \frac{V - P}{R} = G(V - P), \quad (13)$$

we get for the resistance R and the conductivity G a value independent both of the potential V and the time. We chose then for exact measurements the most convenient range of temperatures. In the following two tables, the results of observations on calcite and quartz are shown, both for the direct current and for the opposite polarization current. The accidental errors do not exceed 1 per cent. The potentials $(V - P)$, and P , were measured before the measurement of the current and immediately afterwards. The average was used for the test of equation (13).

TABLE I.—CALCITE

Direct Current

$V - P$	I	$\frac{I}{V - P}$
99.0	53.8	0.543
89.8	48.5	0.542
66.0	35.6	0.541
55.5	30.1	0.542
42.7	23.2	0.541
25.0	13.4	0.538

Polarization Current

P	I	$\frac{I}{P}$
-74.8	-40.3	0.541
-52.7	-28.5	0.542
-34.8	-18.8	0.540
-11.5	- 6.2	0.539

$V - P$	I	$\frac{I}{V - P}$
81.7	43.4	0.535
40.2	22.0	0.543
7.0	3.8	0.543

P	I	$\frac{I}{P}$
-82	-44.5	0.542
-33.6	-18.3	0.543

TABLE II.—QUARTZ

$V - P$	I	$\frac{I}{V - P}$
68	43	0.63
51	35	0.68
36	24	0.67
22	14	0.64
15	9.3	0.62
11	7.4	0.67
10.2	6.5	0.64

P	I	$\frac{I}{P}$
-47	-46	0.98
-38	-32	0.85
-24	-19	0.80
-15	-10.8	0.72

$V - P$	I	$\frac{I}{V - P}$
62	49.5	0.80
44.4	34.0	0.76
35.0	25.0	0.66
24.5	16.0	0.65
14.5	8.8	0.61

P	I	$\frac{I}{P}$
-45	-38	0.85
-31	-24	0.78

We see that the decrease of the direct current and the opposite current are strictly proportional to the measured electromotive force P . We do not, therefore, need any other explanation for the curve of Fig. 28. From these tables the independence of R of the time follows at once and furnishes us with a sufficient basis for the theory of the electrical conductivity of dielectrics. The resistance R , the conductivity G and the specific conductivity σ are then real physical properties of the crystal which can be measured as exactly as any other physical constants.

Practically three methods may be used:

1. The initial current I_o is measured and a test is made to show that at this time the polarization P is still negligible compared to the applied potential V_o . Then it follows that

$$R = \frac{V_o}{I_o}. \quad (14)$$

2. At any time we change the potential by ΔV and measure the change in the current ΔI ,

$$R = \frac{\Delta V}{\Delta I}. \quad (15)$$

3. We measure P directly at a time when dP/dt is small and define R by:

$$R = \frac{V - P}{I}. \quad (16)$$

In the cases where the increase of the polarization is progressing rapidly, fast recording instruments, such as string electrometers, must be used. If necessary, the experiment may be repeated many times for a very short time and the charges given by all experiments may be allowed to accumulate to increase the sensibility.

We were able to test Ohm's law in crystals in regard to the relation between the current and the applied potential difference up to fields producing breakdown. Ohm's law was thus checked for calcite, glass, and mica from a field of 0.1 volt per centimeter up to 5×10^5 volts per centimeter. Applying potentials increasing in an arithmetical progression for 0.1 sec. each, with time intervals of a few seconds between, we measured the corresponding currents by a string electrometer. These were photographed on a moving film and it was found that Ohm's law held for fields as high as 5×10^5 volts per centimeter, if properly applied.

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LECTURE VIII

THE SPECIFIC CONDUCTIVITY

Although the investigation of the passage of electricity through dielectric crystals has established the existence of a definite specific conductivity σ and the methods of its measurement, the value of σ itself apparently cannot be regarded as a property of the substance, but as the property of the given crystalline sample. In fact, several crystals of quartz gave the following conductivities in the direction of the main axis expressed in $10^{-12} \text{ 1}/\Omega$: 8.0; 3.0; 6.8; 1.4; 9.0; 0.9; 0.8; 12.5; and 0.03. The last two values were obtained on colored quartz. Even for seven samples of optically pure and transparent quartz the values differ tenfold. Four samples of ammonium alum furnished conductivities 0.6; 10.8; 36; $0.42 \times 10^{-12} \text{ 1}/\Omega$, differing among themselves by a factor of about 90.

The probable cause of this variation may be suspected as being due to impurities, although the alum crystals were denoted as being "purissimum." According to the experiments of H. Hertz on benzene, such impurities may be removed by the electric current. We tried to purify both the quartz and the alum crystals by a continuous electric current, which was expected to transfer the ions of the contamination to the electrodes. Thereafter the parts of the crystals adjacent to the electrodes were removed and the middle part used for conductivity measurements. We succeeded, in fact, in decreasing the conductivity considerably. A quartz plate which possessed a conductivity of 77×10^{-8} at 200°C . changed its conductivity to a value of 10×10^{-8} as the result of a current acting for 10 hours and reached a conductivity of 1.3×10^{-8} after a treatment by a current at 315°C . This is sixty times less than the initial value. A conductivity of $10.8 \times 10^{-12} \text{ 1}/\Omega$ for an

alum crystal was reduced first to $0.96 \times 10^{-12} \text{ } 1/\Omega$ and finally to $0.22 \times 10^{-12} \text{ } 1/\Omega$ by a prolonged current. It was impossible, however, in this way to reach a constant standard value of conductivity for all crystals of the same kind.

We therefore tried to purify the crystals of ammonium alum "purissimum" by a process of repeated crystallization. We used the best obtainable pure water, dissolved crystals, which were previously examined in a concentrated beam of arc light with respect to possible enclosures and crevices. The surface layer of all dissolved crystals was scratched off by a knife. A continuous and fast stream of supersaturated solution washed the growing crystals which were fastened in glass tubes. After a large number of new crystals were obtained, they were examined in a beam of light. The original crystal, which started the crystallization, and all enclosures were removed and the perfectly uniform pieces of crystals were used for the next crystallization. Four successive purifications by this process were carried out by Mrs. Kirpichewa until a definite result was obtained.

In the following table the results of the conductivity measurements of such crystals are presented. In discussing these measurements we must take into account the possible errors. The most important of them is the influence of the inductive charge appearing on the insulating area between the electrode L and the guard ring G (Fig. 27). For, while the charge liberated on the electrode L is removed by earthing, the charge on the insulating area remains and spreads out over the electrodes L and G during the measurements of the current. If the conductivity is small, this additional charge becomes essential in the first stage of the current. We found that the error became negligible after 2 min., even for the purest crystals. It is of no importance for the better conducting crystals of the initial product after a fraction of a minute. All data in the tables represent the specific conductivity at 17°C. in $10^{-16} \text{ cm./}\Omega$. According to the statement regarding systematic errors, the data of the last columns, which give the current after 2

min., must be considered as the most significant, especially for the crystals of the third and fourth crystallizations.

"PURISSIMUM"

Number	10 sec.	1 min.	2 min.
1	8,000	4,600	4,200
2	1,300	800	700
3	4,200	3,000	2,700
A	36,000	5,000	4,800

I CRYSTALLIZATION

Number	10 sec.	1 min.	2 min.
2	138	42.6	38
4	306	156	120
7	132	27	26
8	225	126	100
18	284	200	138
19	120	48	30
20	222	90	72
21	204	102	60

III CRYSTALLIZATION

Number	10 sec.	1 min.	2 min.
1	55	27	21.0
2	48	22.5	20.6
3	90	24.6	21.8
4	50	27.6	21.6
6	96	33	21.8
7	120	25	22.8
8	108	25	22.2
10	66	22.8	22.2

IV CRYSTALLIZATION

Number	10 sec.	1 min.	2 min.
1	32	23	22.8
2	..	22	21.6
3	..	24	20.4
4	..	23	22.8
A	21.6
B	21.0
C	21.3

Examining the tables, we notice first that the conductivity is decreased by the crystallization and that after the third crystallization the conductivity measured by the current 2 min. after the potential had been applied reaches a standard value 21.6 ± 1.2 , which does not change by the fourth crystallization. The remaining uncertainty of 10 per cent may be largely due to the errors of measurements which are considerable for small crystals and such low conductivities as 20×10^{-16} . The relative errors become, however, smaller at higher temperatures. We chose, therefore, two crystals, No. 2 and No. 10 of the third crystallization, and compared their conductivities at higher temperatures in the same apparatus simultaneously. The following table gives the results, showing that no real difference in conductivities has to be assumed for these crystals. The last column contains data calculated from the formula to be discussed later.

$t^{\circ}\text{C.}$	No. 2	No. 10	Calculated
17	20.6	22.2	20
26	51	49	51
45	455	455	455
63	2,900	2,950	2,900

Crystals No. 5 and No. 9 of the third crystallization gave a high conductivity of about $1,000 \times 10^{-16}$. A reexamination of the crystals revealed crevices going across the crystal between the electrodes. The remaining pieces of these two crystals were, unfortunately, too small to allow an exact measurement and they are, therefore, not included in the table presented. The values were, however, of the right order of magnitude.

We can thus state as a definite result of the measurements that (1) *the data of the last column of the last table represents the true specific conductivity of electrically pure ammonium alum crystals at the corresponding temperatures.*

Analogous experiments were repeated with copper sulfate, sodium nitrate, potassium nitrate, and sodium

chloride, with the same result. A successive crystallization always leads to standard values of conductivity which are less than the conductivity of the original crystals. The following conclusions in addition to (1) may be drawn from these standard conductivities.

2. The water of crystallization (12 molecules in ammonium alum and 7 molecules in CuSO_4) has no influence on the conductivity. As a matter of fact, those crystals are as good insulators as the crystals of NaNO_3 which crystallize without water.

3. Contrary to the results published by F. Braun, the conductivity of crystals crystallizing in *the cubic system* does not depend on the orientation. In fact, among the crystals of the fourth crystallization, the first four plates were cut perpendicular to the direction (100), while the last three were perpendicular to (111). F. Braun found the conduction of rock salt twice as large perpendicular to the (111) plane as for the (100). The table shows that no such dependence exists for ammonium alum, and the same result was obtained for pure crystals of sodium chloride. We may conclude, therefore, that the conductivity of dielectric crystals is a property of the same degree of symmetry as the heat conductivity. It could be represented by an ellipsoid with three different axes for the least symmetrical crystals and by a sphere for the cubic system. The ratio of conductivities for crystals with one or two axes is, however, much higher than for heat conductivity. The coefficients of the heat conductivity differ by 20 to 80 per cent, while the electrical conductivity for such crystals as quartz and calcite in the direction of the main axis is many thousand times higher than in a direction perpendicular to this. The result in regard to the symmetry of the electrical conductivity is not self-evident. As a matter of fact, W. Voigt expected the internal friction which determines the conductivity to have the least possible symmetry so as to be different even for opposite directions for crystals without a center of symmetry.

We next carried out experiments to study the influence of contamination on the conductivity. It was found that a slight contamination of the water used as a solvent with substances such as LiNO_3 , NaCl , $(\text{NH}_4)_2\text{SO}_4$ did not change the standard conductivity if the method of crystallization above described was used. No traces of those substances could be found in the crystals either by chemical analysis or by spectral tests. A contamination by acids, bases, and especially by isomorphous potassium alum considerably changed the value of the conductivity of the ammonium alum crystals. At the same time a change of

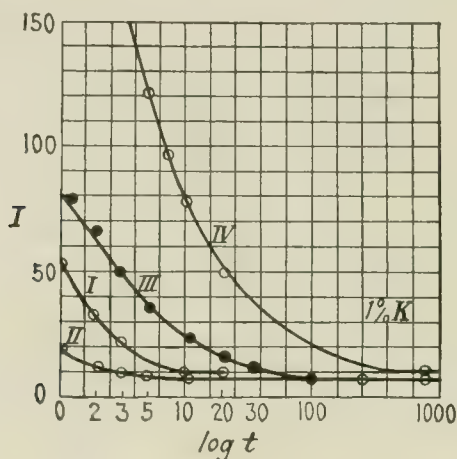


FIG. 29.

another kind was noticed. While the current decreases in pure crystals by but 10 per cent in 24 hours, it decreases rapidly and many times in alloys of ammonium and potassium alum. After some hours, it approaches the value characteristic for pure crystals (20×10^{-16} for ammonium alum and 12×10^{-16} for potassium alum), as shown in Fig. 29.

The decrease of the current down to the values of pure crystals cannot be explained by a purification, because the current used could, according to Faraday's law, only transfer about 10^{-11} gr. of the substance, while the amount of

contamination present reached about 10^{-3} gr. The decrease of the current is presumably due partly to a removal of the superfluous free ions, and partly to the polarization produced by those ions.

The standard conductivity of electrically pure dielectric crystals thus established depends to a great extent upon the temperature, 1°C. increasing the conductivity by 10 to 12 per cent. A rough measurement shows clearly the exponential character of the increase of conductivity with temperature. Two formulae may be proposed: the first, based on an assumption of a heat of dissociation, leads to the form

$$\sigma = \sigma_0 e^{-\frac{\alpha}{T}}, \quad (17)$$

or

$$\log \sigma = -\frac{\alpha}{T} + \beta. \quad (18)$$

The second would be

$$\sigma = \sigma_0 e^{at}, \quad (19)$$

or

$$\text{Log } \sigma = at + b. \quad (20)$$

For a large number of heteropolar crystals equations (17) and (18) were checked with a remarkable accuracy. We have measured quartz, both in the direction of the main axis and in the perpendicular direction, calcite, pure rock salt, fluorite, several nitrates, several alums, and sulfates. All the data except for sodium chloride between 600 and 800°C. agrees with equation (18) in the best possible manner. The same result was found by Tubandt and Lorenz for silver halides. Some of the results are represented in Fig. 30, where $\log \sigma$ is plotted against $1/T$. In this figure I represents the conductivity of calcite; II, III, and IV of quartz parallel to the main axis in different stages of purification; V quartz perpendicular to the axis; VI ammonium alum; VII rock salt; and VIII, IX, X, XI, XII, silver halides.

It is remarkable that for some of the substances, such as NaNO_3 and silver halides, equation (18) holds up to the

melting point. For rock salt, however, the part near to the melting point is better represented by equation (20).

Still more important is the result that the coefficient α in equation (18) has approximately the same value for almost all heteropolar crystals investigated, *viz.*, $1.0 \times 10^4 < \alpha < 1.15 \times 10^4$, in spite of the fact that the chemical type of crystals is quite different. An exception with smaller α seems to be represented by AgI. The coefficient α , representing the slope of the straight lines in Fig. 30 is related

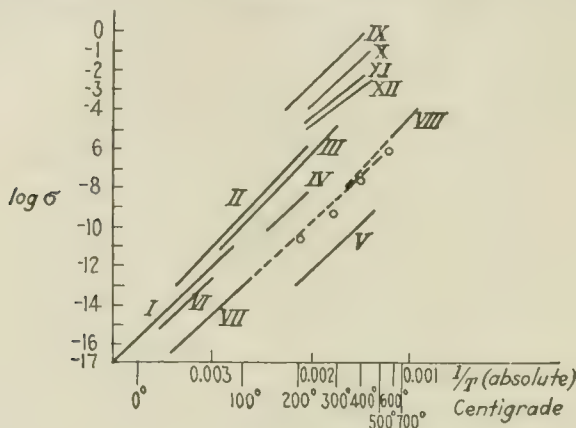


FIG. 30.

to the temperature coefficient K of the conductivity by the relation

$$K = \frac{1}{\sigma} \frac{d\sigma}{dT} = \frac{\alpha}{T^2}, \quad (21)$$

$$KT^2 = \alpha. \quad (21^a)$$

All the crystals shown in Fig. 30 are heteropolar crystals. For lattices of the molecular type such as some non-polar organic crystals, the dependence on temperature and the coefficient α is much smaller, *i.e.*, α is about 0.3×10^4 .

Sometimes it is difficult to measure the true conductivity σ if the polarization increases too rapidly. In this case, the current actually measured corresponds to the final current I_f produced by the difference between the applied potential V and the equilibrium potential P of polarization. The

latter depends upon temperature. Therefore the ratio I_f/V changes with temperature both by the change of conductivity σ and by the change of P . We often find that the ratio I_f/V was used for the conductivity. It may be stated that this ratio can be represented as well by equation (18). The coefficient α then has a different value.

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LECTURE IX

ELECTROLYSIS OF CRYSTALS

The next problem which arises is the one concerning the mechanism of conduction. In the first place, we must know whether a real transfer of charges takes place. Were Curie's superposition law rigidly true under all conditions, we would have to deal with a displacement of charges only. It would even be possible to assume a displacement inside the molecules or the cells of the lattice, which would mean an increasing dielectric polarization instead of a current. It can be shown, however, that such a conception is wrong, although it may be asserted to hold to some extent only at sufficiently low temperatures. Considering the whole scale of temperatures we can certainly neglect this assumption. In fact, while the dielectric polarization and the induced charge remain almost independent of temperature, the conduction current increases rapidly with the temperature and very soon the quantity of electricity carried by the current exceeds the induced charge many thousands or even millions of times. Thus the displacement of charges by the current must take place over a distance a million times greater than the displacement by polarization, even when all charges present are displaced by the current as they are actually displaced by the polarization. If the number of charges displaced by the current is but a very small fraction of the total number of charges in the crystal, which is actually the case, then the displacement must be still greater. There is no doubt, therefore, that the current transfers charges through distances incomparably larger than the atomic distances.

Besides this reason for a real transfer, which is valid even in the domain where the superposition law holds, we find that the superposition law does not hold at all at high

temperatures. The superposition law requires that the opposite current I_p (Fig. 28) must equal the direct current I after a sufficiently long time. Both must become symmetrical with regard to the axis of abscissae, the final value of the current I_f thus reaching zero. This conclusion holds approximately only at low temperatures. With increasing temperatures the ratio of the final current I_f to the initial current I_o increases gradually, as indicated in Fig. 31, representing the $\log I/I_o$ at different temperatures as a function of the time.

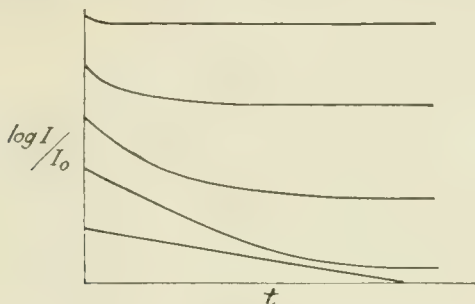


FIG. 31.

Thus, at higher temperatures the opposite current transfers a considerably smaller charge than the direct one. At the high temperatures there is, accordingly, no question about a real net transfer of charges. On the other hand, only a quantitative difference for the ratio I_f/I_o may be observed at different temperatures, and we have no reason for suspecting different mechanisms for conductivity at low and at high temperatures. In fact, it is seen that the same law (equation (18)) connects the conductivities at all temperatures.

We have a still more direct proof of a transfer of charges by the transfer of matter according to Faraday's law. As early as 1888, E. Warburg and Tegetmayer described a transfer of sodium by the current through glass and quartz. Later Haber and Tollutzko produced BaCl on the cathode out of a solid salt BaCl_2 ; Tubandt and Lorenz quantitatively checked Faraday's law on AgCl , AgBr , AgI .

While Warburg and Tegetmayer ascribe their results to a contamination of Na_2SiO_3 in the quartz and while the salts BaCl_2 , AgCl , etc. might possibly conduct over the surfaces of small crystalline grains, I was able to observe the same phenomenon on single "electrically" pure crystals such as AgNO_3 , NaNO_3 , NaCl and alums, by means of chemical and spectral analysis. A transfer of matter by the current through solid dielectrics was found for a great number of different halides, nitrates, sulfates, carbides, for quartz and even for LiH . *There is no doubt that in all these substances we have to do with an ionic conductivity following the Faraday law for electrolytes.*

There are two kinds of difficulties encountered in the quantitative measurements. The first is the influence of contaminations. We observed, for instance, that ammonium alum added as a contamination to crystals of potassium alum was preferentially transferred by the current so that after a prolonged current at 75°C . the content of ammonia was appreciably greater on the cathode side than on the anode side of a crystal. In the experiments of Warburg and Tegetmayer a current through quartz brought sodium into the cathode which did not belong to the lattice of quartz. At higher temperatures, however, a deposit of silicon and a liberation of oxygen from the normal crystal lattice may be observed.

The second and the most important difficulty arises from the fact that the cathode deposit does not build a uniform layer, but produces dendrites penetrating more or less rapidly into the lattice and even reaching the anode. A metallic bridge across the dielectric is thus produced connecting the electrodes and radically disturbing the movement of ions. If the density of the current in these thin bridges is high, they melt and evaporate, producing inside the crystal a fog of colloidal particles, sometimes coloring the crystal red, blue or brown. Those deposits cannot be weighed with the cathode when Faraday's law is being verified and therefore produce an error, which sometimes makes the electrolytic conductivity questionable.

Tubandt noticed that the silver deposited on the cathode of the AgI does not penetrate into the crystal. If AgI is introduced between the cathode and the measured salt, the dendrites in many crystals may be avoided. Tubandt therefore used silver iodide on the cathode in series with the salt to be investigated and was then able to verify Faraday's law and the electrolytic conductivity for many substances. Shukareff used glass in series with rock salt with considerable success for the same purpose. In Fig. 32, some of the dendrites in rock salt taken without glass are shown, as seen in a microscopic section many times enlarged.

Faraday's law was checked, using these precautions for many multicrystalline salts to an accuracy of 0.1 per cent.

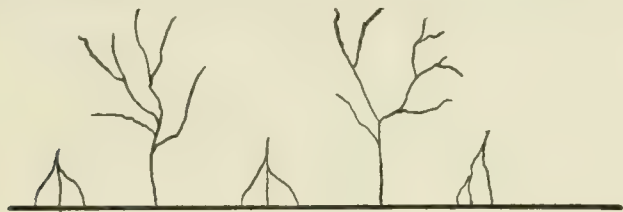


FIG. 32.

P. Lukirsky was able to reach an accuracy of 1 per cent even with pure single crystals of rock salt and calcite. It is thus shown that the conductivity in these cases is a purely electrolytic one. There are some oxides in which the mechanism of the conductivity is yet uncertain. All transparent dielectric crystals which were carefully investigated turned out, however, to be electrolytes.

We will later discuss cases where conduction by electrons liberated by light or ionizing rays was proven to exist, even in crystals where the heat agitation produces ions only.

We may next consider the question of the transference numbers for the ions. The question has been solved by the same method that is used for liquid electrolytes, that is, by separately weighing the electrodes with the adjacent parts of the substance. Tubandt and Lorenz found, contrary to the case in liquids, that in solid dielectrics the

differences in mobilities are so large that practically only one kind of ion is mobile. This difference may reasonably be ascribed to the fact that the ions of a crystal are not surrounded by a cloud of the molecules of the solvent and that the free space between the ions of the lattice is limited. In most of the halides, the mobile ion was positive; for PbCl_2 they found, however, that the negative chlorine ion is the only mobile one. Lukirsky proved that in single crystals of rock salt and calcite at least 99 per cent of the current is carried by the positive Na^+ and Ca^{++} ions. The circuit in these experiments was composed of three polished crystalline plates which were pressed together. In order to prevent decomposition of CaCO_3 it was enclosed in marble. The center crystal changed its weight only to the extent of the evaporation of NaCl or of the CO_2 . The other two plates, weighed together with the electrodes, revealed a transfer corresponding exactly to the transfer of metallic ions according to the Faraday law.

The results of mobility measurements agree well with the fact that the same ions were found to be displaced by diffusion inside the crystal lattice and by evaporation in a vacuum.

While it is then obvious that the current in pure dielectric crystals is due to a transfer of the ions of the crystal lattice, several possible hypotheses present themselves to account for the origin of the mobile ions. I have assumed that the heat agitation removes some of the ions from the equilibrium positions to which they are bound elastically in the crystal lattice to a distance at which the elastic force is zero, or very small. Such ions I considered as free ions, capable of moving under forces exerted by the weakest electric fields, with an average velocity proportional to the field, while the normal ions are only slightly displaced by the field, and produce a dielectric polarization of the crystal. The relative number of the free ions is small as long as we are far below the melting point. It increases rapidly, however, on approaching the melting point. The

cell which has lost its ion is destroyed, and a new equilibrium of the remaining ions is established there. The potential energy of ions in such a cell is different, generally higher than for normal cells, and, therefore, dissociation proceeds more easily in such cells. If one of the ions in its motion by chance comes near enough to such a destroyed cell to be attracted, it may replace the removed ion and restore the normal lattice. It may also happen that before a new ion approaches, the dissociation of the distorted cell progresses further and a permanent change, sometimes even a hole, is produced. As a matter of fact, Lukirsky noticed a great number of holes of microscopic dimensions after an electrolysis of long duration in rock salt.

Concerning the mechanism of the transfer of ions, two hypotheses may be made: either (1) the free ions move between the ions of the crystal lattice subjected to some frictional resistance due to the irregular heat movements and collisions, or (2) the ions only move to refill the empty place liberated by the ions ahead of them, so that rows of ions replacing each other are built between the electrodes. The experiments concerning the transfer of foreign ions through a lattice described below seem to indicate that the first hypothesis is the more probable one.

If the picture of free ions suggested above is correct, we must represent the specific conductivity σ in terms of the degree of dissociation D and the mobilities of the ions v_1 and v_2 by the equation:

$$\sigma = DNe(v_1 + v_2), \quad (22)$$

where N denotes the number of ions of one sign per cm.³ and e the charge of the ion. For most of the crystals investigated one of the mobilities can be neglected and the equation may be written in the form

$$\sigma = DNe v. \quad (22^a)$$

While the degree of dissociation will depend on the probability of large amplitudes or accidental coincidence of phases of the heat movement in a manner similar to the

dissociation of molecules in a liquid, a different mechanism must be assumed for the recombination. A free crystal-line ion becomes bound, in general, not by a collision with an ion of the opposite sign, but by approaching a cell vacated previously by an ion of the same sign. The probability of a recombination is, therefore, proportional to the product of the density of ions present and the degree of the dissociation of the lattice at this place, and not to the product of the densities of ions of both signs actually present. The theory of such a dissociation has been worked out by Frenkel.

The assumption described above is not the only one proposed or possible. Another assumption suggested some years ago by Hevesy makes use of the analogy to a melted salt, where all ions take part in the conduction of the current. For some salts the jump of conductivity at the melting point is not exceedingly high, and Hevesy assumed that the change is due to the drop of the mobility, while the number of ions does not change materially. Thus, the degree of dissociation is almost unity. This hypothesis, however, appears to fail to account for the fundamental Ohm's law. The ions of the crystal lattice are bound elastically and thus some definite minimum force and work are necessary to remove the ions from the equilibrium position and displace them to an appreciable extent, and we have shown above that a considerable displacement actually does take place.

One conclusion may be drawn from the assumption that all ions of the lattice participate equally in the current. On Hevesy's picture we would expect that a sufficiently weak field will not suffice to pull out the ions and will thus produce a negligible current, while a high field will enable all ions to partake in the current and thus produce a disproportionally high current. Instead of Ohm's law, the hypothesis would lead to a very small current for weak fields, which increases suddenly at some higher field. Contrary to this conclusion, Ohm's law was checked over the whole domain of possible fields, even more completely than the Joule law.

The most convincing proof of the existence of a definite degree of dissociation is given in the next lecture, where the number of free ions is shown to increase after heating.

A second hypothesis, due in a general form to Hevesy, which has been extended and defended by Smekal in recent times, ascribes a fundamental rôle in the conduction to a distortion of the crystal lattice by irregularities in spots of the dimensions 10^{-6} cm., which were introduced during the crystallization. According to this hypothesis in its most definite form, no heat dissociation takes place except at such weak spots. The degree of the irregularity is thus responsible for the degree of dissociation.

Many objections arise if we seriously consider the hypothesis as a general explanation of the conductivity and not merely as a factor becoming of practical importance in special cases. First of all, it is hardly conceivable that hundreds of separate crystals, crystallized in the above described fashion, can give the same conductivity within 1 per cent, if this conductivity is due to accidental irregularities. This uniformity of conductivity among different samples of the same crystals is found as soon as all chemical impurities are removed from the crystals and seems to be independent of the process of crystallization and physical regularity. At higher temperatures we get standard values, even in the presence of small amounts of impurities.

A second more important objection to this theory is based on the negative result of measurements of the influence of artificially produced irregularities in a crystal.

There is no doubt that the conditions on the surface of the crystal are more favorable for dissociation than inside the crystal, because the heat of dissociation there is about half as great. Therefore a solid dielectric, such as compressed powder with a large surface on the numerous particles, will conduct better than a single crystal as long as the surface is clean and free. It is, however, not certain to what extent the conductivity will be influenced by the irregularities inside the lattice if no change in the density is involved. If the picture of Smekal were right, we might

expect that such a distortion of a crystal lattice would considerably increase the conductivity. To prove this E. Zeehnowitz tried to compare the conductivity of a single crystal with its conductivity after a plastic deformation which resulted in a distortion of the lattice into an agglomeration of minute crystals in actual contact, without absorbed gas layers and free surfaces inside. The conductivity of a pure rock-salt crystal was measured at 400 to 500°C. while it was subjected to a gradually increasing compression. No change of specific conductivity exceeding 1 per cent was noticed even after a high plastic deformation of more than 10 per cent in the external size had been produced. At this stage the single elements had a magnitude of about 10^{-5} cm. The number and the magnitude of irregularities were undoubtedly much larger than the normal irregularities in a well-formed single crystal. Thus we have no reason to believe that the influence of the hypothetical invisible irregularities were predominant when even a visible distortion of a still higher magnitude was not able to affect the specific conductivity by as much as 1 per cent.

We may look for indications as to the nature of the actions producing dissociation by considering the temperature coefficient of conductivity. The specific conductivity σ is determined by the number n of ions in a cm.³ of the crystal and by their mobility v .

$$\sigma = nev.$$

The number of ions produced by heat agitation at an absolute temperature T must be determined by the energy u necessary to liberate an ion of the crystal lattice.

$$n = Ne^{-\frac{u}{kT}}, \quad (23)$$

where N represents the total number of the ions in a cm.³ considered, and k the Boltzmann constant.

Unfortunately, the mobility v is also a function of the temperature. In the case of quartz v was separately measured and represented either by an equation

$$v = v_0 e^{-\frac{S}{T}}, \quad (24)$$

where

$$S = 0.65 \times 10^4,$$

or by the equation $v = v_0 e^{pt}$, which is similar to equation (19). Another way of estimating the dependence of v on temperature may be drawn from the diffusion measurements in crystals made by Hevesy. This would for rock salt lead to a value of S of about 10^3 .

The average value of S for liquid dielectrics is about 10^3 .

Considerations of the mean free path, according to the data given in Lecture 16 would lead to a still smaller value for S .

Comparing equations (23) and (24) with equation (17) for the conductivity we find:

$$\alpha = \frac{u}{k} + S, \quad (25)$$

$$\sigma_0 = N v_0. \quad (26)$$

Assuming for α the value 10^4 and for S , 10^3 , we may compute u .

$$u = k(\alpha - S) = 1.37 \times 10^{-16} \times 0.9 \times 10^4 = 1.24 \times 10^{-12} \text{ ergs.}$$

On the other hand, we computed the energy u_0 of the normal ions of the crystal lattice

$$u_0 = -\frac{A}{r} \left(1 - \frac{1}{n} \right),$$

where $A = 1.75 e^2$, $n = 10$, and $r = 2.81 \times 10^{-8}$.

$$u_0 = 1.28 \times 10^{-11} \text{ ergs.}$$

This quantity is about ten times larger than u . In comparing these values, however, it must be remembered that the energy u_0 of the ion is not the same as the dissociation energy u of the same ion. In computing u_0 we assumed that the ions of the lattice were removed from the lattice (that is, from the proximity of other ions) *into a vacuum*. The energy u represents the work necessary to remove one ion of the lattice from its normal position of minimum energy to some average position *inside the same lattice*. For two reasons, therefore, the work u must be considerably

less than u_o . The first reason is that in removing the ions which move freely inside the lattice into a vacuum we must do additional work. Denoting the dielectric constant of the crystal by ϵ and assuming that the average distance from the free ion to the ions of the lattice be d , we find the energy of the electric field surrounding the ion in the crystal starting at a distance d and extending to infinity to be given by $u_k = e^2/2\epsilon d$, while the same field in vacuo will have a higher energy $u_v = e^2/2d$. The work which must be applied is thus

$$u_v - u_k = \frac{e^2}{2d} \left(1 - \frac{1}{\epsilon} \right). \quad (27)$$

The most uncertain quantity in this equation is the actual value of d . Assuming, for instance, that $d = 2 \times 10^{-8}$ cm., and $\epsilon = 5.6$, we obtain

$$u_v - u_k = 0.46 \times 10^{-11},$$

a value of the same order of magnitude as u_o itself.

For rock salt the smallest d would correspond to half the distance between the ions $d = 1.41 \times 10^{-8}$ cm. Thus the upper limit for $u_v - u_k$ is $u_v - u_k < 0.66 \times 10^{-11}$. The highest value for d is the distance from the center of a cell to the corner $d = 2.4 \times 10^{-8}$ cm. Thus the lower limit for $u_v - u_k$ is

$$u_v - u_k > 0.39 \times 10^{-11}.$$

The average value of $(u_v - u_k)$ is 0.52×10^{-11} . Using this value, we find the work necessary for the removal of an ion from its equilibrium position to a free average position in the lattice to be $u_o - (u_v - u_k) = 1.28 \times 10^{-11} - 0.52 \times 10^{-11} = 0.76 \times 10^{-11}$ ergs.

A second correction must be added to account for the change in the polarization energy of the surrounding ions. The removal of the ion diminishes the polarization and therefore the energy of the ions of the former cell of the ion. Half of the work applied to remove the polarization energy of the system must be done on the polarization energy of the cell itself. The highest limit for this energy

is half of the work applied to change the position of the ion. This polarization correction is

$$u_p \leq \frac{0.76}{2} \times 10^{-11} = 0.38 \times 10^{-11}.$$

The expected value for the work which must be done by the heat agitation in order to make one ion of the crystal lattice free is thus less than 0.38×10^{-11} ergs, or 3.8×10^{-12} ergs, which is about three times the value of u calculated from the temperature coefficient.

Taking into account the uncertainty of the corrections and estimations made with respect to S , u_k , and u_p , we cannot ascribe any great importance to the numerical agreement in its present uncertain form. It, however, makes the liberation of normal ions by heat a possible assumption, which needs more verification.

It must be mentioned that for a considerable number of crystals, such as NaCl, CaF₂, AgCl, AgBr, and TiCl, the energy of the ion u , and the dissociation work u are numerically closely the same. All those crystals possess the same temperature coefficient of conductivity $\alpha = 10^4$.

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LECTURE X

DISSOCIATION IN QUARTZ

While electrolytic dissociation and conduction are common to almost all dielectric crystals, the manifestation of these phenomena is found to vary considerably, depending on the nature of the crystal investigated. We will therefore discuss the behavior of crystals separately for three general types, characterized by their best representatives: quartz, calcite and rock salt.

The most fruitful application of the mechanism of heat dissociation described may be found in the properties of quartz and mica, which belong to the same class in this respect. The first information concerning the phenomena produced by the passage of an electric current may be found from a study of the potential distribution in the crystal. Quartz possesses a conductivity many thousands of times greater in the direction of the principal axis than in a direction perpendicular to this. Therefore I used a plate cut parallel to the principal axis, this being the direction of the current. At seven places between the electrodes graphite strips were drawn on the surface around the quartz plate. A switch which could connect these seven electrodes with seven electrometers of small capacity at a given instant enabled one to measure the potential in the corresponding cross-sections of the quartz plate, as shown in Fig. 33. These electrometers are charged by a current perpendicular to the main axis, where the conductivity is small and where the opposite electromotive force of polarization is easily produced by the most minute current. This would introduce an error increasing with the charge transferred to the electrometer. In order to avoid this error, the electrometers were previously charged to almost the expected potential. The switch was operated to ascertain

whether the charge was too high or too low. After a few such trials, I succeeded in bracketing the potential in the seven cross-sections between sufficiently close limits with-

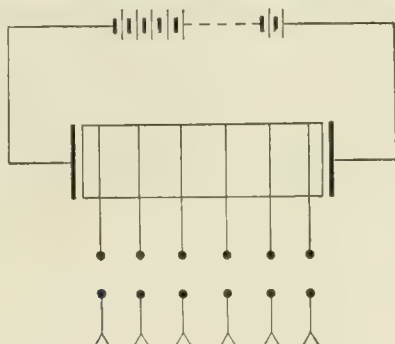


FIG. 33.

out drawing any appreciable charge from the quartz plate. A proper choice of the temperature used (about $150^{\circ}\text{C}.$) permitted me to finish a measurement of the

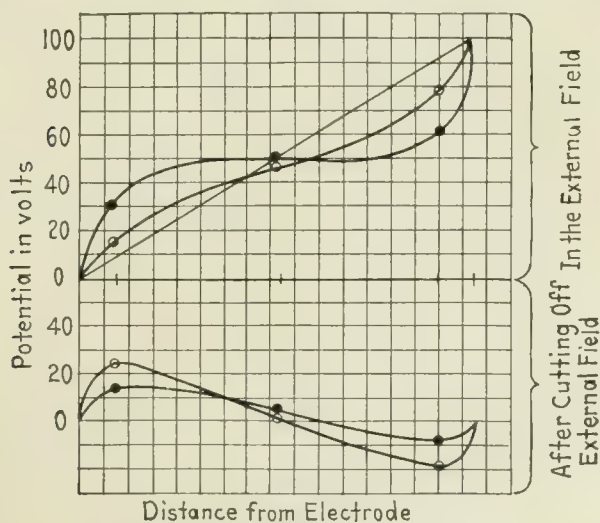


FIG. 34.

potential distribution within a time during which the conditions could be considered as stationary. The following diagrams (Fig. 34) show the distribution of potential

both for the direct and the polarization current. The straight line shows the potential distribution actually found a few seconds after the field had been applied. This is a good test of the homogeneity of the quartz plate in its initial state. Later measurements show alterations, indicating an appearance of space charges (Fig. 34). They are diffusely distributed over a considerable portion of the crystal. The magnitude of these charges can be easily computed from the curvature of the curves. The change of the charges with time allows us to compute the displacement current, which was, however, small relative to the current actually measured on the plate. We conclude, therefore, that the current is mostly due to conduction. If so, the potential distribution gives a means of measuring the conductivities in different sections of the plate. The specific conductivity is obviously inversely proportional to the slope of the potential curve in the corresponding section.

Denoting the number of positive ions in a cm.³ by n_+ and the number of negative ions by n_- , we may use a relation which is true for every section: to wit,

$$\frac{d^2V}{dx^2} = \frac{-4\pi}{\epsilon} (n_+ - n_-)e, \quad (28)$$

where ϵ is the dielectric constant of quartz. Further denoting the corresponding mobilities by v_+ and v_- we have also:

$$\frac{dV}{dx} = \frac{-I}{(n_+v_+ + n_-v_-)e}, \quad (29)$$

where I is the current measured.

We must remember that these equations neglect the displacement current. For the final potential distribution corresponding to an equilibrium produced by a given potential difference, the displacement current disappears completely and equations (28) and (29) are accurate. During the period when the equilibrium is being reached, the displacement current must, however, be considered. It is especially important for the polarization current where an

equilibrium distribution leads to the absence of a field and of a current. Assuming that the same distribution holds independently of the thickness of the plate, we will consider a case where the area of the cross-section is very large compared to the distance between the electrodes. The charge in a slab of thickness dx and of unit cross-section will be $e(n_+ - n_-)dx$. The current produced by the change of this charge in the whole crystal of the thickness D will be:

$$i = e \int_0^D \frac{d(n_+ - n_-)}{dt} dx = eD \int_0^D \frac{(n_+ - n_-)dx}{dt}. \quad (30)$$

If the total charge of the quartz plate during the formation of the polarization were continuously zero, the displacement current would be zero. This would be especially true for a symmetrical potential distribution curve. I ascertained, however, that the distribution is not symmetrical. The asymmetry is not due to a heterogeneity of the quartz plate because, on changing the direction of the current, I always observed a higher charge on the cathode side, independent of the part of the crystal used as cathode. Thus we have some evidence either for the existence of a displacement current or for the inequality of the mobilities v_+ and v_- or for both. We might, from the measurements, expect the mobility of the negative ion to be slightly higher than that of the positive one.

In the final distribution, the conductivity is greatest in the middle part and decreases gradually approaching the electrodes. The space charge is greatest at the electrodes and diminishes towards the center.

The alteration of the potential distribution in quartz is exactly analogous to the well-established theory of ionic conduction in gases at high pressures. We will, therefore, assume a similar mechanism of conduction and recombination of ions of both signs in quartz. The various phenomena described below agree quite well with such an assumption.

Considering the superfluous ions producing the space charge in a field, we find that they have less opportunity of

recombining with oppositely charged ions, than the ions in the absence of a field. For, neglecting the difference in mobilities v_+ and v_- , we conclude from equation (28) that, when approaching the negative electrode, $(n_+ - n_-)$ becomes larger, while $(n_+ + n_-)$ becomes smaller. Thus the number of the negative ions drops in this region far below the normal density. The recombination of a positive ion by collision with a negative ion, or the probability that a positive ion meets a crystalline cell lacking a positive ion, if we accept that picture of the dissociation and recovery of the crystal lattice, is proportional to the product $n_+ \times n_-$. This product will diminish in this region in direct proportion to the number of negative ions or cells deprived of positive ions actually present. The ions stored up in the neighborhood of the electrodes will be preserved from recombination. On the other hand, the dissociation could hardly be influenced by the electric field or depend upon the number of free ions present. The equilibrium between dissociation and recombination will consequently be displaced and the actual number of the corresponding ions will exceed the normal density. Most of these ions are near to the opposite electrode. If, however, we change the direction of the current, they are available throughout the whole crystal. By the polarization current such separated and preserved ions will be distributed more or less uniformly over the crystal and will produce a temporary superfluous conductivity. A new current will separate them once more and bring the conductivity to the original value. This consequence of the picture we have adopted was checked by the measurements given in the following tables corresponding to Table I of Lecture VII checking Ohm's law for calcite. Here V is the applied potential which is constant, and P is the increasing potential due to polarization. $V - P$ thus decreases and represents the true potential causing the flow of the current I which decreases as P increases. The resistance $(V - P)/I$, however, remains constant.

TABLE I.—DIRECT CURRENT

$V - P$	I	$\frac{I}{V - P}$
68	43	0.63
51	35	0.68
36	24	0.67
22	14	0.64
15	9.3	0.62
11	7.4	0.67
10.2	6.5	0.64

TABLE II.—POLARIZATION CURRENT

P	I	$\frac{I}{P}$
-47	-46	0.98
-38	-32	0.85
-24	-19	0.80
-15	-10.8	0.72

TABLE III.—DIRECT CURRENT

$V - P$	I	$\frac{I}{V - P}$
62	49.5	0.80
44.4	34.0	0.76
38.0	25.0	0.66
24.5	16.0	0.65
14.5	8.8	0.61

TABLE IV.—POLARIZATION CURRENT

P	I	$\frac{I}{P}$
-45	-38	0.85
-31	-24	0.78

Figure 35 shows the current as function of time in a quartz plate when 100V and 0V were applied alternately. The increase of conductivity is obviously manifested by the increase of the jump of the current with successive changes of potential.

In absence of a field, the superfluous conductivity disappears in time by recombination, as shown in Fig. 36.

The horizontal straight line indicates the normal conductivity of the plate. The experiment extends over 190 hours. The time scale, however, varies considerably with temperature. At 100°C. the same decrease would be

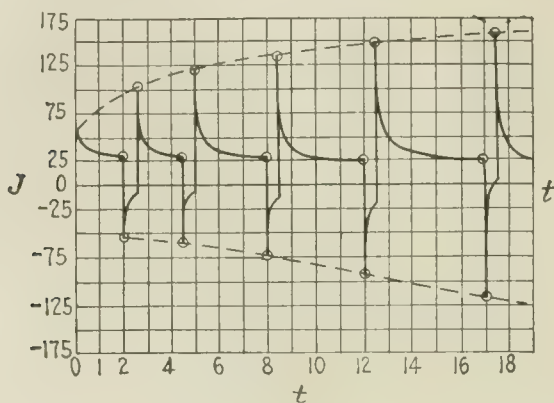


FIG. 35

obtained within 1 hour only, that is, two hundred times faster. The increase of the conductivity at this temperature would be about ten thousand times.

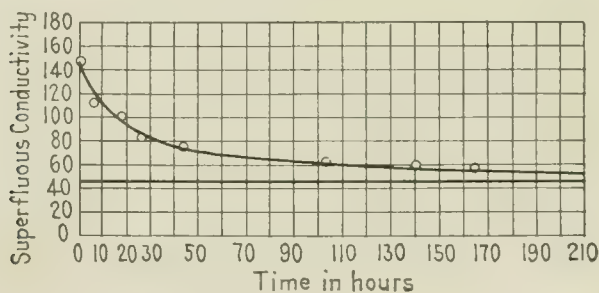


FIG. 36.

If the explanation given above is true, the thermal equilibrium in quartz must be approached with a speed indicated in Fig. 36. This must be true for any superfluous ions, whatever their origin may be. We found, in fact, that any increased conductivity produced by heating or by the

influence of ionizing rays disappears in the same way. Shaposhnikow checked the coincidence of the curves, showing the decay of the conductivity which had been artificially increased by the current, by heating, by ultra-violet light, and by X- and radium-rays. As might be expected from a retarded approach to a normal equilibrium, the new equilibrium corresponding to a steady illumination by light or by radium-rays is also reached asymptotically after many weeks. It must be stated that the sensitiveness to a further illumination is less after such a treatment, as if the ionized substance in quartz had recombined to a less sensitive substance, or modification.

This phenomenon of a retarded equilibrium was used in order to distinguish the effects of the degree of dissociation from the effects of the mobility on the conductivity. If a quartz plate be suddenly cooled, say from 100°C. to 0°C., it will retain the degree of dissociation corresponding to 100°C., while the mobility will presumably correspond to 0°C. At 100°C. an artificially produced conductivity will decrease to half of the initial excess value after about 5 min. At 0°C. it takes about 30 hours. Using a quartz plate of a thickness of about 0.2 mm. and copper electrodes of high conductivity, Shaposhnikow was able to cool the quartz plate in less than 1 min. Under these conditions we may neglect the decrease of the dissociation during this time.

We denote by σ_{100} the conductivity at 100°C., by σ_0 the conductivity at 0°C., and by σ_0^{100} the conductivity of the plate suddenly cooled from 100 to 0°C. The relative change of the degree of dissociation between 0 and 100°C. will be then

$$\frac{D_{100} - D_0}{D_0} = \frac{\sigma_0^{100} - \sigma_0}{\sigma_0}, \quad (31)$$

and the relative change in mobilities:

$$\frac{v_{100} - v_0}{v_0} = \frac{\sigma_{100} - \sigma_0^{100}}{\sigma^{100}}. \quad (32)$$

Using this method, these quantities were investigated. It was found that both the dissociation and the mobility may be expressed between the temperatures 0 and 100°C., either in the form

$$\log D = at + C, \quad (33)$$

$$\log v = a_1t + C_1, \quad (33^a)$$

or

$$\log D = -\frac{A}{T} + B, \quad (34)$$

$$\log v = -\frac{A_1}{T} + B_1. \quad (34^a)$$

The dissociation D and the mobility v are related to the specific conductivity σ by the equation

$$\sigma = nev = DNe v, \quad (35)$$

where N is the total number of ions in a cm.³, which is almost independent of temperature.

We have represented the conductivity by the equation

$$\log \sigma = -\frac{\alpha}{T} + \beta = \log D + \log v + \log N \cdot e. \quad (36)$$

Comparing equation (36) with equations (34) and (34^a) we find:

$$A + A_1 = \alpha. \quad (37)$$

Shaposhnikow found

$$\begin{aligned} A &= 0.5 \times 10^4, \\ A_1 &= 0.65 \times 10^4, \\ \alpha &= 1.15 \times 10^4. \end{aligned}$$

According to these data, the dissociation increases in quartz less rapidly with temperature than in rock salt. If the dissociation of a quartz crystal has been highly increased by radium rays, we may assume that in raising the temperature we will influence the mobility only, while the number of free ions may be considered as constant. Thus the conductivity will depend on temperature by an amount given by the change in mobility with temperature only. In fact, the temperature coefficient of the conductivity of quartz with artificially increased conductivity was found to be 0.7×10^4 instead of 1.15×10^4 .

If we could find either the number of ions or the mobility at some temperature, we would be able to find both at any temperature. The number of ions may be estimated from the increase of conductivity due to the ions stored up in the neighborhood of the electrodes. In one experiment it was found, for instance, that the conductivity increased four times after the ions were distributed uniformly over the interior of the plate. The total number N of the additional ions of each sign was computed from the potential distribution by the relation

$$N = \int_0^D n dx = - \int_0^D \epsilon \frac{d^2 V}{4\pi e} dx = \frac{\epsilon}{4\pi e} \left[\left(\frac{dV}{dx} \right)_0 - \left(\frac{dV}{dx} \right)_D \right], \quad (38)$$

where ϵ denotes the dielectric constant of quartz. The average density of the ions of one sign was found equal to 2×10^9 , while the number of elastically bound ions is about 2.7×10^{22} per cm.³. Hence the degree of dissociation turns out to be about 7×10^{-14} at 17°C. For the mobility ($v_+ + v_-$), we would then obtain 5×10^{-7} cm./sec.

We could use the same experiment to compute the mobility directly. A nearly uniform distribution of the stored ions was reached after 10 min. in a plate of 2 mm. thickness by a potential of about 150 volts. This leads to a mobility of about 1×10^{-6} cm./sec. Other experiments made to reach a saturation current showed that a field of 20,000 volts cm. removed the ions in 3 sec. from a quartz plate about 0.5 mm. thick. This corresponds to a mobility of about 7×10^{-7} cm./sec.

The order of magnitude of the values of mobilities obtained in different ways was found to be the same. Assuming that this value is approximately correct, we can compute the mobility v and the dissociation D at different temperatures. The result of such a computation is given in the following table.

T abs.	D	ν
290	7×10^{-14}	5×10^{-7}
600	8×10^{-10}	1×10^{-3}
900	2×10^{-9}	3×10^{-2}

Remembering how different the conductivities of single samples of quartz crystals are, we must consider the data given in the table as indicating the order of magnitude only.

If we assume for the recombination of ions the law:

$$\frac{dn}{dt} = -\alpha n^2,$$

and use the curve in Fig. 36 for the decrease of n we will find the coefficient of the recombination α equal to about 12×10^{-16} . The number of ions n_0 produced during a second by heat dissociation must then be

$$n_0 = \alpha n^2 = 12 \times 10^{-16} \times (2 \times 10^9)^2 = 5 \times 10^3 \text{ per sec. per cm.}^3 \text{ at room temperature.}$$

Besides a recombination of the ions, we must also consider their diffusion when, in the problems considered, their distribution is not uniform. The ions stored up by an electric field in the neighborhood of the electrodes which produce an opposite electromotive force of polarization are thus subjected to recombination and diffusion. An equilibrium is reached when the number of ions transferred into the polarized sheets becomes equal to the number removed by diffusion and recombination. This equilibrium gives the maximum polarization. With increasing temperature, diffusion and recombination increase rapidly and therefore the maximum polarization decreases. Thus the final residual current grows relative to the initial current. Accordingly, the relative decrease of the current by polarization becomes less at higher temperatures until at temperatures beyond 600°C . the polarization ceases to play an important role in the conductivity of quartz. This explains the disappearance of the initial decrease of the conduction-current curves shown in Fig. 31 of Lecture

IX. The properties of quartz discussed above, though very roughly measured, give a consistent picture which may be applied with the same success to mica and some sorts of glass, which also exhibit all the phenomena described.

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LECTURE XI

CONDENSED POLARIZATION CHARGE IN CALCITE

It was found that a group of crystals, best represented by calcite, showed properties in an electric field, which were quite different from the above-described behavior of crystals like quartz. A production of superfluous ions through heating, by means of a current, or by the action of radium rays, raises the conductivity of quartz and mica for a long period of time after the removal of the ionizing source. The normal dissociation equilibrium is therefore reached only after many months following such treatment. Contrary to this behavior of quartz, the normal conductivity and, therefore, the normal dissociation seems to be reestablished in calcite within a small fraction of a second. Assuming in calcite the same phenomena of dissociation and recombination as in quartz, we may easily compute that the coefficients of diffusion and recombination must have a value at least 10^5 times larger than in quartz at the same temperature.

While X-rays and radium rays gradually increase the conductivity of quartz until a new equilibrium with higher dissociation is reached, the calcite shows a different behavior. The conductivity decreases slowly under the direct action of X-rays and there is apparently no production of new mobile ions. The charges produced by X-rays seem to be attached somewhere inside the crystal. Their return by way of diffusion is accompanied by the emission of a reddish phosphorescent light which is emitted for a long time after the exposure to X-rays has ceased. At room temperature phosphorescent light may be noticed even after 10 days. At higher temperatures the decay of phosphorescence is faster. The emission of light is over after 40 min. at 70°C . It was found that the temperature coefficient of phos-

phorescence agreed with the temperature coefficient of conductivity. The intensity I of the light emitted by calcite at a time t after illumination ceased may be represented by the equation

$$I = I_0 e^{-\gamma t}$$

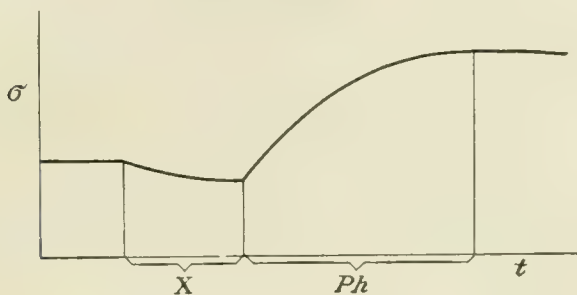


FIG. 37.

The coefficient γ measures the velocity of the decay of phosphorescence. On expressing it by an equation of the form

$$\gamma = -\frac{A}{T} + B, \quad (40)$$

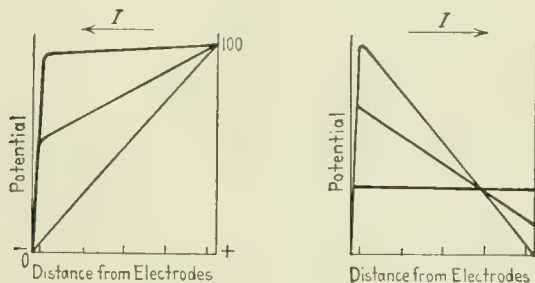


FIG. 38.

we find for A almost the same value 1.1×10^4 , which is characteristic for the conductivity of calcite.

During the period of phosphorescence and apparently by the same process, the conductivity of calcite increases to an extent proportional to the light energy already emitted. The total amount of light emitted and the final increase of the conductivity seem to be independent of temperature. Figure 37 shows the change of the conductivity during the

exposure of X-rays (indicated by X) and during the following period indicated by Ph , when phosphorescence only is present.

After a new equilibrium is reached the conductivity begins to decrease once more, but this time very slowly—about 10 per cent a year. This process, too, may be accelerated by heating. After 2 hours at 200°C . the conductivity drops considerably. The interpretation of these results, which have unfortunately not been carried much further, remains obscure.

The most important phenomenon found in calcite is a peculiar kind of high-voltage polarization concentrated on one electrode. The measurements of the potential distribution similar to the experiment indicated by Figs. 33 and 34 yielded a different result for calcite than was found for quartz. The drop of potential corresponding to the polarization and the space charges was concentrated in a thin layer on the cathode side of the current. No charges were found either on the anode side or between these two points. Figure 38 shows the distribution measured both for the direct current and for the polarization current at different times after the current began.

The initial distribution is a straight line, proving the uniformity of the crystal. At any moment the potential is given by a straight line except near the cathode. The final distribution indicated by the heavy line shows a vanishing gradient throughout the whole thickness of the crystal, except for a thin layer at the cathode, where the whole potential difference of polarization appears. The polarization current is first produced by this potential difference. Then the potential of the polarization diminishes, while a new polarization is built up on the opposite side, which is now the cathode for the polarization current. The final state corresponds to some positive potential inside the crystal with two equal drops of potential at the two electrodes.

The drop of potential at the electrode represents the electromotive force of polarization denoted above by P (equation (13)). Equation (13) says, that subtracting P

from the applied potential V , we get the potential difference over the remaining portion of the crystal, which is proportional to the current flowing through it. Thus the resistance of the main body of the crystal is not changed by the current, the change being limited to the thin layer near the cathode only. We may thus conclude that if this layer were removed, the changes produced by the current would wholly disappear.

In fact, by grinding off the surface which was used as cathode to a depth of 0.01 mm. it was possible to remove all traces of polarization. A grinding of the anode had no effect at all. By careful polishing Lukirsky was able to show that the thickness of the polarized layer was limited

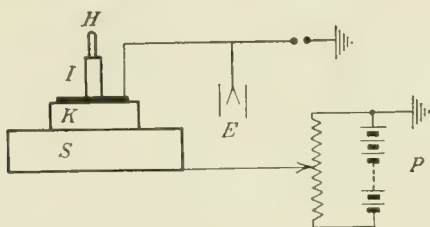


FIG. 39.

to a few wave lengths of light. A complete investigation of the polarized sheet was carried out by Sinelnikov. He was able, not only to measure the thickness of the polarized layer, but also to measure the distribution of potential inside the layer. He did this by gradually removing the layer by polishing off thin sheets of about a quarter of one wave length. The thickness of the sheet removed was measured either by a Zeiss microscope or by interference fringes. It is important that one prevent a displacement of the polarization during the process of the polishing. The diffusion of charges may be retarded by lowering the temperature. The removal of charges by currents was prevented by the arrangement shown in Fig. 39.

The cathode side of a calcite plate K was ground on a large cold-steel plate S . An amber insulator I separated the second electrode connected to an electrometer E from

the earthed handle H . The steel plate was charged by means of a potentiometer P to such a potential that the electrometer E remained steadily at a zero potential. Thus no current could flow during polishing. From time to time the thickness was measured, while the corresponding potential was given by the potentiometer.

In this way potential distribution curves for the thin cathode layer were obtained consisting of five to six measured points. Those curves were repeatable and independ-

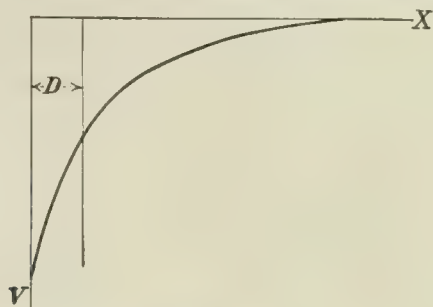


FIG. 40.

ent of the speed of the grinding process. Figure 40 shows such a distribution curve on a large scale. In logarithmic representation, the curve turned out to be a straight line, following the equation

$$V = V_0 e^{-\alpha x}. \quad (41)$$

Assuming that equation (41) really represents the curve of Fig. 40, we may compute the field E and the density of the space charge ρ as a function of x .

$$E = \frac{dV}{dx} = -\alpha V_0 e^{-\alpha x}, \quad (42)$$

$$\rho = \frac{\epsilon}{4\pi} \frac{d^2 V}{dx^2} = \frac{\epsilon \alpha^2}{4\pi} V_0 e^{-\alpha x}. \quad (43)$$

On the other hand,

$$\rho = e(n_+ - n_-), \quad (44)$$

where n_+ the number of positive ions in cm.^3 must be regarded as constant, and n_- as a function of x , if we assume that the negative ions are the only mobile ones. This is possible as dissociation is small and the negative ions are

the only mobile ones. The density of the negative ions is then

$$n_- = n_+ - \frac{\epsilon\alpha^2}{4\pi e} V_o e^{-\alpha z} \quad (45)$$

The polarized cathode layer thus represents a continuous space charge of the positive electricity (*i.e.*, the excess of positive electricity), distributed according to equation (43). This charge is balanced by a corresponding negative charge bound on the negative metallic electrode. The negative electrode and the positively charged layer together represent a condenser of capacity C , equal per unit surface to

$$C = \frac{\int_0^\infty \rho dx}{V_o} = \frac{\epsilon\alpha}{4\pi}. \quad (46)$$

We may replace this space-charge condenser by a parallel-plate condenser of the same capacity C , where the whole charge $\int_0^\infty \rho dx$ is considered as distributed in a plane at a distance D from the electrode. For a surface of 1 cm.², the capacity of such an imaginary condenser is

$$C = \frac{\epsilon}{4\pi D}. \quad (47)$$

Comparing equation (47) with equation (46), we find the thickness D of the imaginary condenser, which represents the thickness of the polarized layer, to be

$$D = \frac{1}{\alpha}. \quad (48)$$

It was found that the distribution shown in Fig. 40 and in equation (41) is an equilibrium distribution. It remains almost the same from 2 min. to 24 hours after the field has been applied. Therefore the displacement current can be neglected relative to the conduction current. It follows further that the slope of the curve (Figs. 38 and 40) at any point is inversely proportional to the specific conductivity and presumably to the number of mobile ions present at that point. On studying Fig. 33 we must conclude that both the total conductivity and the specific conductivity

of the polarized layer are very small compared with the conductivity of the normal crystal, where the gradient of potential is very small for the same steady current (*i.e.*, the current which is flowing through the whole crystal). The current therefore produces on the cathode a layer with a conductivity which rapidly decreases as we approach the electrode, according to equation (42), and with a positive space charge increasing in the same direction according to equation (43). This layer is characterized by two parameters: P , the potential of polarization, and $\alpha = 1/D$ representing the inverse thickness of an equivalent condenser.

We showed in Lecture VII how P can be measured and will now give the methods used for the measurement of α . As we concluded from a study of Fig. 38, the resistance of the polarized layer measured by the potential difference in this layer is many times (possible many thousands of times) higher than the resistance of the remaining part of the crystal which is measured by the potential difference over this part. We may, as a first approximation, therefore, neglect the conductivity of the polarized layer, and consider it as a non-conducting condenser with a capacity given by equations (46) and (47). We may assume that the current I measured in the crystal goes to charge this condenser to the potential of polarization P . We have, thus, the relation,

$$Idt = CdP. \quad (49)$$

Ohm's law gives, according to equation (13),

$$\frac{dI}{dP} = -\frac{I_o}{V_o} = -\sigma, \quad (50)$$

where I_o is the initial current and V_o the applied potential. Combining equations (49) and (50), we have

$$\frac{dI}{I} = -\frac{1}{C} \frac{I_o}{V_o} dt = -\frac{\sigma}{C} dt, \quad (51)$$

$$\log \frac{I}{I_o} = -\frac{\sigma}{C} t \quad (52)$$

$$I = I_o e^{-\frac{\sigma}{C} t}. \quad (53)$$

Plotting $\log I$ against time we may therefore expect a straight line, and the capacity C would be given by the angle α (Fig. 41) which this line makes with the axis of ordinates.

$$C = \frac{1}{\sigma} \tan \alpha = R \tan \alpha. \quad (54)$$

Experiment shows that the first part of the curve $\log I = f(t)$ is actually represented by a fairly straight line. The capacity C has, therefore, a definite value.

Another method was proposed by D. A. Roshansky. Instead of using a constant potential difference a constant current I is used. The potential difference applied to the crystal is continuously changed in a way necessary to maintain a constant current.

If a manual adjustment by means of a potentiometer becomes impossible, due to the rapid increase of the polarization, the saturation current in a vacuum tube with a heated filament which is connected in series

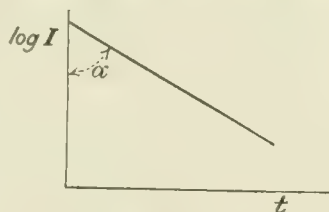


FIG. 41.

with the crystal may be used to achieve this. The current is, under the latter circumstances, limited and defined by the temperature of the filament. We can then measure the potential difference across the crystal as a function of time. At every instant the relation given by equation (13) must hold, that is,

$$\frac{V - P}{R} = I = \text{constant}.$$

Therefore

$$dP = dV. \quad (55)$$

Using equation (49) we obtain

$$C = I \frac{dt}{dV}, \text{ or } \frac{dV}{dt} = \frac{I}{C} \quad (56)$$

If C is constant during the production of the polarization layer, since I is also constant, the dependence of V upon time must be represented by a straight line making an

angle β with the axis of ordinates. This conclusion was checked by numerous experiments. Figure 42 represents the increase of V with time. From this it is obvious that

$$C = I \tan \beta. \quad (57)$$

A third method consists in connecting the polarized electrode to a condenser of a known capacity and measuring the change of potential produced, compared to the potential of the insulated electrode. A measurement of the potential distribution as described above is, of course, the most direct but also the most difficult method for determining α and D .

All four methods described gave identical results after the polarized layer was built up. The initial current applied to a normal crystal gave a capacity three to four times larger than that from subsequent charge and discharge experiments, when equations (54) and (57) were used. This is adequately accounted for if we remember that the first current finds the polarized layer in the normal state of high conductivity. The first current must, therefore, remove the ions from this sheet by a current flowing

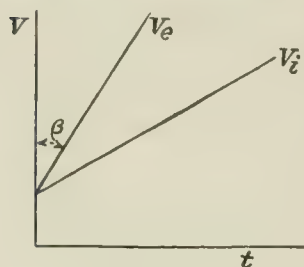


FIG. 42.

through the whole crystal. The current I consists, in this case, of two parts: (1) a conduction current through the polarized sheet, and (2) a current charging the condenser C . The second part only can be used in equations (54) and (57). In Fig. 42 the line V_i represents the first polarization and V_e the equilibrium case of a completely formed non-conducting sheet. The thickness of the polarized layer actually corresponds to the line V_e , and has a value between 0.5μ and 10μ .

The capacity given by equations (54) and (57) applies to 1 cm.^2 of the surface. It must, however, be remembered that the thickness of the polarized layer is of the order of magnitude of 1μ . Every irregularity of the surface

greater than 1μ must be considered as a new surface. We must thus plot the surface on a scale corresponding to 1μ in order to obtain a proper value for the surface of the polarization condensers. Thus a ground surface cannot be represented by a plane with the same area. It has a much larger area. A well-polished surface where the depth of the irregularities does not exceed a quarter of a wave length of light may, however, be considered as a plane.

The thickness of the polarized layer $D = 1/\alpha$ was remarkably constant during the charging and discharging of a given calcite crystal. For different samples the values of the capacity C vary between 500 and 10,000 cm. For the same sample, the capacity increases slowly with temperature between 17 and 180°C . It is nearly independent of potential between 10 and 2,000 volts, and increases slightly with the current.

Studying different dielectrics, we found a number of them, such as Boron oxide and certain carbonates and sulfates, which showed the same properties as calcite. The capacity was found, however, to be highly influenced by impurities.

The distribution of space charges found in dielectrics of the type of calcite is to be explained by an equilibrium of two tendencies: (1) the electric field which tends to move the mobile ions (in calcite, the negative ions) from the polarized layer to the opposite electrode; (2) an opposite tendency, such as a diffusion, must be responsible for a tendency to move the ions back. An equation consistent with the experimental results may be derived from such an assumption. The usual coefficient of diffusion, which can be expressed by the mobility and the absolute temperature, is, however, many hundreds of times too small to explain the highly concentrated polarization of thousands of volts.

Led by the hypothesis that the polarized layer is a very poor conductor, we have assumed that the positive space charge is produced, not by superfluous positive charges which are for some reason not able to move very far, but

by a space charge due to a lack of mobile negative ions, these ions having been removed by the field. Now, contrary to expectation, the measurements of transference numbers for calcite at temperatures as high as $600^{\circ}\text{C}.$, where the polarization disappears, led to the result that under these conditions the mobile ions are the positive Ca^{++} ions. If the conductivity and the polarization observed at low temperatures were due to the ions coming from the CaCO_3 itself, we would have little reason to expect the negative ions to be mobile at low temperatures. We found on a study that calcite crystals of American origin, possessing a conductivity many hundreds of times less than Iceland calcite, did not show the polarization phenomena observed on the better-conducting Iceland calcite. Chemical analysis indicates that Iceland calcite has some impurities (Mg and Fe) which are absent in the American calcite. It seems justified, therefore, to assume that the polarization at the cathode is due not to the few movable positive Ca^{++} ions, but to the more numerous negative ions of impurities. This assumption is supported by the fact that high polarizations (over 2,000 volts) which, according to equation (45), remove a large number of negative ions from the polarized layer, permanently change this layer. The number of negative ions of the impurity actually present in a thin layer, and which may be removed, is not sufficient to produce such high potentials. Thicker layers of space charge are then required to increase the polarization potential over 2,000 volts. Under such conditions, the thickness increases gradually with the polarization potential; all movable ions are removed and no thermal equilibrium can be established. The ions, therefore, do not return after the removal of the electric field, as would be expected and as has been observed for space charges governed by an equilibrium between the electric field and a diffusion proportional to the gradient of the density of ions. After a treatment with a high polarization, the thickness of the non-conducting layer in Iceland calcite remains the same, even for low potentials,

and the conductivity of this layer drops below the conductivity of the American calcite.

It is probable that the final current flowing through the crystal and through the polarized sheet is due to the positive Ca^{++} ions of the lattice. This final conductivity of the polarized sheet, which becomes independent of potential at polarizations of about 2,000 volts, is ten thousand times less than the normal conductivity of Iceland calcite. If we ascribe this remaining conductivity to pure calcite, we

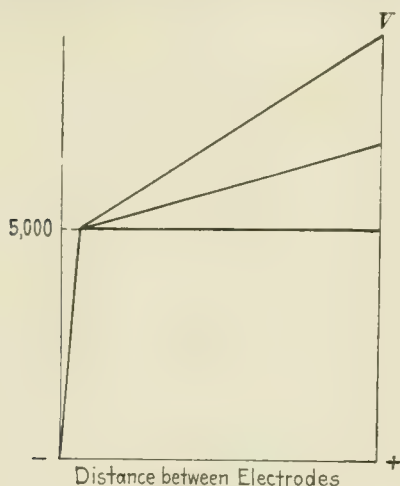


FIG. 43.

must conclude that the normal conductivity is largely due to impurities, and probably to the negative ions.

Increasing the polarizing potential still more, we find some maximum of about 5,000 volts which cannot be surpassed. The distribution of potential shown for this case in Fig. 43 leads to the conclusion that the conductivity of the polarized layer begins to increase. We will later discuss the explanation of this phenomenon on the basis of the mechanism of ionization by collision.

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LECTURE XII

ELECTRONIC CONDUCTIVITY

While all phenomena so far considered have been due either to ions of the crystal lattice or to ions of some contaminating substance, we shall now take up the phenomena which are due to the electrons liberated in the lattice of a dielectric crystal. In 1903, I happened to find the first instance of the electronic type of conductivity in such crystals, while studying the influence of Röntgen rays upon the conductivity of various crystals. While the conductivity of quartz, calcite, and many other crystals increased distinctly under the influence of *X*-rays, the measurements on rock salt yielded utterly irregular and inconsistent results until I noticed that clouds covering the sun caused a diminution in the conductivity, in spite of the fact that the attempt to find an effect due to visible light on natural rock salt had failed completely. Rock salt first exposed to *X*-rays or radium rays, however, was found to become sensitive to visible light to such an extent as occasionally to increase the conductivity about 10^6 times the conductivity in dark. Rock salt thus sensitized to light by treatment with *X*-rays furthermore takes on a yellow-brown color indicating an absorption in the visible spectrum. This increase in conductivity by light will be shown to be due to electronic carriers.

I then studied these electronic phenomena in collaboration with W. C. Röntgen. P. Lukirsky and A. Arseneva later carried out these investigations. The careful and extended work of R. Pohl, B. Gudden, and Z. Gyulai, who, in several crystals had found the same phenomenon and investigated it, has done much to clarify the problem.

The conductivity of rock salt is not markedly increased by *X*-rays, but they make it sensitive to visible light and

cause it to absorb light. The sensitivity may be measured by the current produced by a given source of light after or during the exposure to *X*-rays. Both the sensitivity and the absorption increase with the amount of *X*-ray energy absorbed by the crystal. After the removal of *X*-rays the sensitivity gradually decreases. At room temperature and without light, a high sensitivity and a brown coloring still remained as long as 21 years after treatment. Heating or illumination of the crystal accelerates the decrease considerably. If we regard the influence of *X*-rays on conductivity apart from light we must remember that the phosphorescent light produced by the absorbed *X*-rays increases the conductivity and accelerates the process of the disappearance of the sensitivity. The phosphorescent light may be noticed many minutes after the removal of the *X*-rays.

Besides rock salt, the same behavior was found for sylvine, fluorite, and for all the alkali halogens studied. These phenomena are closely connected to the properties of the photographic silver halides in which Arrhenius discovered the increase of the conductivity under illumination as early as 1887.

In a given state of activation the conductivity produced by light is strictly proportional to the intensity of the light and takes place immediately (in less than 10^{-4} sec.). The illumination by light also has a slowly progressive secondary effect, increasing the absorption and sensitivity for the red end of the visible spectrum. This effect may be removed, as shown by R. Pohl and B. Gudden, by an exposure to infra-red light or by heating to between 60 to 100°C. This secondary effect of light has maximum value independent of the intensity of the light used.

The primary effect of *X*-rays is probably a production of neutral sodium atoms inside the crystal lattice; the secondary effect may be ascribed to a distortion of the crystal lattice in the neighborhood of the ionized points of the lattice.

Siedentopf was able to observe ultramicroscopic sodium particles both in the blue-colored rock salt produced by reduction at high temperature in hydrogen, and the natural blue rock salt. Although the brown crystals do not show particles of even ultramicroscopic size, the analogy in the behavior leads one to suppose that neutral sodium atoms are also present in a still finer state of subdivision. The color is not due to any contamination, as it may be produced in the chemically purest crystals. It is brown for rock salt and violet for potassium chloride.

The influence of light may be explained by the well-known photoelectric properties of sodium and potassium. While a free surface of sodium in vacuum possesses a photoelectric wave length limit of about 5800 Å., the limit must be still lower for sodium particles in a medium of the dielectric constant 5.6 corresponding to rock salt. Thus, photoelectrons must be liberated by visible light from such atoms in the crystal treated by X-rays, and the electrons carry the electric current if they are mobile in the crystal lattice.

In fact, we have evidence that the conductivity of the illuminated rock salt is due to electrons in contradistinction to the ionic conductivity of the normal crystals. While the ionic conductivity decreases at low temperatures and becomes too small to measure for most dielectrics and especially for rock salt at liquid air temperatures, the conductivity produced by light is practically unchanged by a cooling to the liquid air temperature. It is thus more convenient to work at liquid-air temperatures as the normal dark conductivity of rock salt vanishes at those temperatures and the only current observed is that due to light.

A still more convincing proof is furnished by the Hall effect observed by P. Lukirsky (1916). He was able to show that the current produced in rock salt colored by the action of X-rays under the influence of light, is deflected by an intense magnetic field in a direction corresponding to a current carried by free electrons. The free path of

electrons calculated from these measurements comes to about 10^{-6} or 10^{-5} cm. The Hall effect may be definitely regarded as a proof of the electronic nature of the conductivity, as it could never be observed where conduction was electrolytic and could hardly be expected for ionic carriers if the free path is assumed to be of a reasonable length.

With a given intensity of light, the electronic current is proportional to the potential difference applied. Thus Ohm's law is observed to hold up to 10^5 volts per cm. Assuming that the number of electrons liberated by light is independent of the external electric field, we may assume that, in order to account for Ohm's law, either (1) the average velocity of electrons moving through the crystal is proportional to the field (as is the case for ions in an electrolyte or electrons in a metal); or (2) as R. Pohl has done, that electrons are transferred a short distance only by the field. In the latter case, we should be obliged to

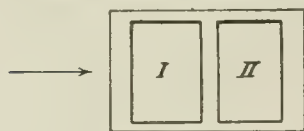


FIG. 44.

set these distances strictly proportional to the field, and make them independent of temperature. It is obvious that Pohl's assumption introduces complications whose explanation is difficult.

The dependence of the conductivity upon the wave length of the light was measured by two methods. It might be expected that only absorbed light would be able to liberate electrons and increase the conductivity of the activated rock salt. It was desirable, therefore, to relate the conductivity to the amount of light energy absorbed in the crystal. In the first method, I used a well-polished plate of colored rock salt and sent sunlight reflected from a Rowland grating through the plate in the direction indicated by the arrow in Fig. 44.

Two separate electrodes I and II measured the photocurrent at two successive sections of the plate. The area of the electrodes was adjusted in such a way that the currents I_I and I_{II} through both electrodes were equal if illuminated in a direction at right angles with the arrow.

The intensity of light in the spectrum of a Rowland grating was taken from Langley's data. The coefficient of absorption α was approximately determined by the ratio:

$$\alpha = \frac{I_I - I_{II}}{I_I}.$$

With an average error of about 10 per cent it was found that the photocurrent through the electrode I was proportional to the energy of light absorbed over the whole visible spectrum independent of the wave length.

More accurate measurements were carried out by A. Arseneva. Light from a Pointolite lamp of 1,000 cp. and of a mercury arc lamp were concentrated on the slit of a spectroscope. A narrow section of the convenient wave length was separated from the spectrum and concentrated on the slit of a second spectroscope. The contamination due to diffuse light in the second spectrum was thus reduced to a negligible extent. The energy of this light J was measured by a Rubens linear thermoelement. Immediately before and after the measurement of the conductivity the absorption coefficients were determined by means of a photoelement. In order to avoid the error produced by reflection at the surface of the crystal, a second crystal of the same size and shape cut out from the same piece of rock salt was used. It was adjusted so that the absorption of both crystals was equal before the exposure to X-rays. One of those crystals was then activated by X-rays and colored brown. The same light which served for conductivity measurements passed through either the colored crystal or the transparent one and fell on the photoelectric cell. Denoting the photoelectric current in the first case by I_c and in the second by I_t , we determined the absorption coefficient α

$$\alpha = \frac{I_t - I_c}{I_t}.$$

The measurement of the conductivity σ included a correction for the electromotive force of space charges. The secondary effects were excluded by illumination with

infra-red light according to the method suggested by R. Pohl.

The curve for the conductivity σ as a function of the wave length is represented in Fig. 45 by the full line, the curve representing the absorbed energy by the dotted line. Within the experimental errors of 5 to 7 per cent the ratio

$$\frac{\sigma}{\alpha J} = \text{constant}, \quad (58)$$

was independent of the wave length.

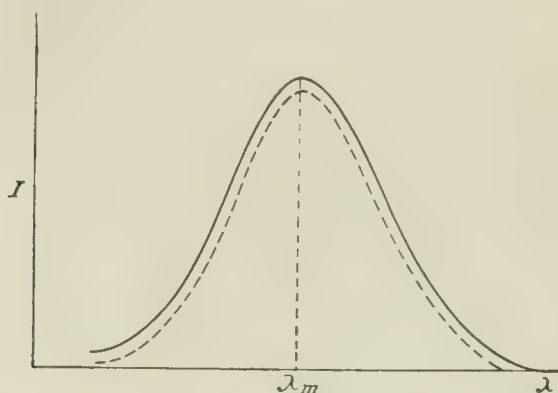


FIG. 45.

Simultaneously with these experiments, Gyulai, using a similar method, found a result which seems to be different, namely,

$$\frac{\sigma}{\alpha J} = K\lambda. \quad (59)$$

The same ratio as above is now proportional to the wave length of the light.

From experimental point of view, however, the disagreement between equations (58) and (59) is not very large. Both equations agree in the statement that the highly pronounced maximum sensitivity in the spectrum is due to a maximum of absorption. While equation (58) gives for both curves in Fig. 45 a symmetrical shape, equation (59) causes the full curve to be slightly rotated relative to the dotted curve. The conductivity corresponding to

shorter wave length must be less and for longer wave lengths greater than in Fig. 45.

Accurate measurements may be made only in a small domain of the spectrum lying in the neighborhood of λ_m . Therefore, in practice, the difference between equations (58) and (59) just exceeds the highest possible experimental errors.

Equation (59) might have a definite physical interpretation. Assuming (1) that every absorbed quantum of light energy $h\nu$ produces one electron, (2) that independent of the initial velocity of the liberated electrons the conductivity is only proportional to the number of electrons primarily produced, and (3) the coefficient of proportionality between these is independent of the wave length, we can deduce equation (59). The first assumption was checked from the photoelectric saturation current in crystals like diamond, where the number of electrons liberated from the crystal lattice could be directly measured. It is questionable, however, whether the assumption may be justified in the case of colored rock salt. It is very probable that the sodium produced by X-rays is not distributed largely in the form of single atoms, but is partly concentrated in small aggregates of atoms, which may still remain invisible in an ultramicroscope. Such particles will at the usual surface give a photoelectric effect, which is not proportional to the absorbed energy. It is well known that the number of electrons escaping from the surface per unit of absorbed light increases with increasing frequency of light, contrary to the implication contained in equation (59). Furthermore, a selective photoelectric effect might be expected from the surface effect on sodium particles. Both these conclusions were verified on blue rock salt which possesses the higher degree of coagulation that is easily noticeable in the ultramicroscope. If the same effect were present, though to a smaller extent, in the brown rock salt colored by X-rays, the effect would be that both curves in Fig. 45 would be more symmetrical, corresponding to equation (58).

It was further assumed that the current carried the primary electrons liberated by light only. As the ratio of the energy $h\nu$ to the minimum energy producing an electron is often larger than 2, it is possible that besides those primary electrons secondary electrons liberated by the primary ones may appear in the same way as through the absorption of X-rays in air. If the secondary electrons were to play an important role, we could determine the total number of free electrons as the ratio of the absorbed energy to the average energy necessary to liberate one electron. This picture would then correspond to equation (58).

In pure crystals of sulfur, I found a second type of the electronic conductivity produced by light without a previous activation by X-rays. From the domain of the strong absorption in the violet down to longer wave lengths, the absorbed light increased the conductivity up to as much as 10^6 times. Observations contrary to this effect were due to the use of opaque aggregates of sulfur crystals instead of a transparent single crystal.

A complete and conclusive investigation of this type of crystals has been carried on by R. Pohl and B. Gudden on diamond, zinc sulfide, and selenium. Contrary to the case of rock salt, a complete saturation current can be observed, thus allowing one to compute the absolute number of electrons produced. If one part of the path of the current only was illuminated, the saturation current corresponded to the energy absorbed in this part. Measuring the absorbed light energy U and the number of electrons N transferred by the saturation current, Pohl and Gudden found

$$N = \frac{U}{h\nu}, \quad (60)$$

that is, one electron per absorbed light quantum. Equation (60) was checked in a domain between the strong absorption band of the diamond in the ultraviolet down to longer wave lengths. It seems to fail for shorter wave lengths.

The current removing negative electrons charges the crystal positively. Thus, a secondary current produced by

the space charge follows the primary current. A heating or an illumination with infra-red light increases the secondary current. It presumably does this by increasing the conductivity through a liberation of positive ions.

A behavior analogous to diamond was found in all dielectric crystals with a refractive index exceeding 2. The high refractivity indicates, as expected, a low ionization energy of electrons in the crystal lattice. It is especially satisfactory that Pohl and Gudden succeeded in clearing up the problem of the photoelectric conductivity of the selenium which, because of its practical importance, was repeatedly studied and created quite an extensive and inconsistent literature.

The phenomena of the photoelectric conductivity are obviously closely connected to the phenomena of phosphorescent and fluorescent light, the investigations of which seem to be decidedly simplified by the use of pure single crystals.

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LECTURE XIII

PHOTOELECTRIC EFFECT OF DIELECTRICS

Ultraviolet light produces electronic conductivity in dielectric crystals and therefore liberates electrons inside the lattice. This internal photoelectric effect does not necessarily lead to an external effect. After the electron is removed from its normal quantum orbit in the lattice, additional work must be applied to pull it out from the lattice into vacuum. We must therefore expect that the minimum frequency ν_p of the light able to produce an external photoelectric effect will be greater than the minimum frequency ν_c which increases the conductivity. The difference $\nu_p - \nu_c$ must give the frequency which is able to remove free electrons from the crystal.

$$\nu_p - \nu_c = \nu_f. \quad (61)$$

Equation (61) can be verified as all three frequencies can be measured. Furthermore, the values of ν_p and ν_f may also be roughly calculated.

The external photoelectric effect was measured by two different methods. The first method, which I worked out in 1912 for measuring the elementary photoelectric effect on small particles, is equally applicable to any substance conducting or insulating. The action of gravity on small charged particles is balanced in the electric field of a condenser of the type used by Millikan and Ehrenhaft. As long as the charge of the particle does not change, it remains stationary for many hours. If, however, the particle be illuminated by light which is able to remove one electron, the equilibrium of the electrical and the gravitational forces no longer exists and the particle begins to move. In practice, the measurement of the wave-length limit for the photoelectric effect requires an energy which exceeds the

intensity given in the ultraviolet by a monochromator. We were therefore obliged to use the sparks between several different metal electrodes and a system of filters, cutting off light of frequencies above a given limit.

P. Lukirsky, L. Kulikova, and N. Gudris worked in this way on 16 different crystalline salts and found for the wavelength limit of the photoelectric effects the data presented in the following table. The limiting wave length was enclosed between two values, except for crystals like CdBr_2 and LiF , where the limit is below the absorption limit for air. The data of the third column represent in volts the probable threshold of the photoelectric effect and the fourth column gives the energy of the ion of the crystal lattice.

Crystal	Limiting wave length λ	Probable limiting energy in volts	Energy of an ion of the crystal lattice in volts
NaCl	$2,026 > \lambda > 2,000$	6.2	7.9
KCl	$2,026 > \lambda > 2,000$	6.15	7.2
RbCl	$2,062 > \lambda > 2,026$	6.1	7.0
CsCl	$2,062 > \lambda > 2,026$	6.05	6.7
CuCl	$1,930 > \lambda > 1,860$	6.6	10.3
NaBr	$2,062 > \lambda > 2,000$	6.15	7.3
KBr	$2,062 > \lambda > 2,026$	6.05	6.7
CuBr	$2,026 > \lambda > 1,930$	6.3	9.7
CdBr_2	$1,860 > \lambda$	> 6.7	13.2
NaI	$2,062 > \lambda > 2,018$	6.1	6.8
KI	$2,170 > \lambda > 2,062$	5.8	6.2
RbI	$2,250 > \lambda > 2,170$	5.6	6.0
CsI	$2,250 > \lambda > 2,170$	5.6	5.8
LiF	$1,860 > \lambda$	> 6.7	11.0
NaF	$2,000 > \lambda > 1,860$	6.6	9.6
RbF	$2,000 > \lambda > 1,860$	6.4	8.5

Thus the energy required for the removal of an electron is always less than but of the same order of magnitude as the energy of the corresponding negative ion.

The considerable influence of the surface conditions upon the threshold of the photoelectric effect made it desirable to measure the effect in vacuum on a fresh

surface. The chief difficulty arises from the low conductivity which makes the actual potential on the free surface of the dielectric uncertain.

P. Tartacovsky, who performed these experiments, used one of the two following arrangements (Fig. 46): The crystal was fixed on a silver-coated glass tube which was either heated by a platinum filament or cooled by liquid air. In the first case the conductivity increased to assure uniform potential in the whole crystal; in the second case

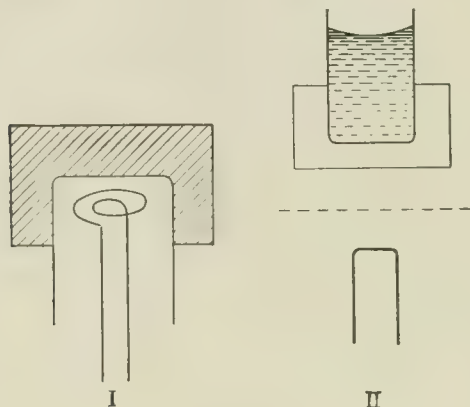


FIG. 46.

we could regard the crystal as an ideal insulator. It is a satisfactory feature of the measurements that they checked the results obtained on small particles in air within the experimental errors, showing thus that the adsorbed air has not as high an influence as in the case of metals.

P. Tartakovsky and I. Dorfman also measured the threshold for crystals activated by X-rays and illuminated by blue light. Those crystals doubtless have free electrons which are able to move inside the lattice and carry the current. It was found that an external photoelectric effect cannot be observed for wave lengths greater than 3200 \AA. , corresponding to the energy of a quantum of 3.9 volts. Assuming that this value corresponds to the work necessary to pull out a free electron from the metal, we

conclude from equation (61) that the work V_c necessary to liberate an electron inside the lattice ought to be

$$V_c = V_p - V_f = 6.2 - 3.9 = 2.3 \text{ volts.}$$

This energy corresponds to a wave length 5400 Å. It is impossible, however, to observe any conductivity produced even by light of 2700 Å. in pure untreated rock salt. An experimental limit for light-producing conductivity in rock salt is still unknown. The same is true for the photoelectric conductivity of crystals like diamond. Light of longer wave length than the absorption band liberates electrons in a number corresponding to the absorbed energy. The longer the wave length the farther it is from the absorption maximum and the smaller, therefore, the absorbed energy and the number of free electrons. There is no evidence that the liberation of electrons ceases at some frequency when light is absorbed by the same band. In rock salt a considerable absorption begins at 1500 Å. only, which corresponds to 8.3 volts. Therefore no internal photoelectric conductivity should be detectable below this limit. It may be, however, that this limit is given not by the energy required to liberate an electron, but by the absence of absorption. This explanation is supported by comparison with the ionization energy calculated for a free isolated chlorine ion—5.2 volts. We should expect that in a substance like rock salt with a dielectric constant $\epsilon = 5.6$ the energy would be considerably less than 5.2 volts.

Equation (61) includes the assumption that in the photoelectric effect the same light quantum removes the electron from its orbit and pulls it out of the crystal. The possibility that one quantum liberates the electron while a second pulls it out should also be considered. If so, the condition for the external photoelectric effect would be

$$\begin{aligned} \nu_p &> \nu_c, \\ \nu_p &> \nu_f, \end{aligned} \tag{62}$$

instead of equation (61).

Taking into account the fact, however, that the number of photoelectrons is proportional to the intensity of light

and not to the square of it, as it should be, and that the free electrons become bound in a time less than 10^{-4} sec., this hypothesis seems to be improbable for small intensities of light.

Another explanation for the failure of equation (61) is given by the possibility that only surface electrons are pulled out by light. It is easily shown that the energy required must be considerably less for surface electrons. We are not yet able to calculate exactly the energy difference for an electron removed from the lattice into vacuum. The radial field of the electron polarizes the ions inside the crystal in a complicated way, creating not only dipoles but also moments of higher degrees. Nevertheless, for a rough computation we may replace the crystal by a uniform substance with the dielectric constant ϵ , which was measured in a uniform field and which, therefore, refers to induced dipole moments only. We may further assume that the field is diminished about the electron starting from some minimum distance r_o , corresponding to the next shell of ions. Inside the sphere with the radius r_o the field is not influenced by the substance as this space is free.

Thus the energy of the field inside the crystal except for the small sphere r_o is

$$U_i = \frac{1}{8\pi\epsilon} \int_{r_o}^{\infty} \frac{e^2}{r^4} 4\pi r^2 dr = \frac{e^2}{2\epsilon r_o}. \quad (63)$$

The energy of the same part of the field outside the crystal

$$U_o = \frac{e^2}{2r_o}. \quad (64)$$

The energy difference is then:

$$U = U_o - U_i = \frac{e^2}{2r_o} \left(1 - \frac{1}{\epsilon}\right). \quad (65)$$

Expressing U by the potential difference V which gives to the electron the same energy, we obtain

$$U = \frac{e^2}{2r_o} \left(1 - \frac{1}{\epsilon}\right) = e \frac{V}{300},$$

$$V = 150 \cdot e \frac{\epsilon - 1}{\epsilon r_o} = 7.13 \times 10^{-8} \frac{\epsilon - 1}{\epsilon r_o} \text{ volts.} \quad (66)$$

For rock salt $\epsilon = 5.6$; if r_o be measured in 10^{-8} cm.,

$$V = \frac{6}{r_o} \text{ volts.} \quad (67)$$

To assign a value to r_o , we assume that it is less than the distance from the center of an undeformed cell to the corner and larger than half the distance between the two next ions, which is 2.81 \AA .

$$1.4 < r_o < 1.4\sqrt{3}.$$

We thus obtain

$$2.5 < V < 4.3 \text{ volts.} \quad (68)$$

The value $V_f = 3.9$ volts, for the energy required to pull out a free electron from rock salt is thus consistent with the calculated limits. We must remember, however, that the assumption used in those calculations could hardly be justified and shall therefore not ascribe very much importance to the numerical agreement.

It is obvious from the calculation that no matter what the real value of V_f may be, it will be almost twice as large for internal electrons as for surface electrons, because in the latter case we would have to consider half the space surrounding the electron instead of the whole space.

In order to experimentally find the work necessary to remove surface electrons, P. Tartakovsky covered the surface of a non-activated crystal of rock salt, which was rendered non-conducting by cooling to liquid air, with electrons which had received a small energy, 2 to 5 volts. He next assured himself that no traces of electronic conductivity inside the crystal were caused by these electrons, and hence that they did not penetrate into the crystal. For crystals coated with electrons in such a fashion, a wave-length limit of 3100 \AA . was found. This is almost identical with the limit for free electrons liberated from the surface of rock salt. Thus the minimum energy required to remove electrons which are made free by an activation by X-rays and an illumination with blue light is equal to the energy required to pull out electrons deposited on the surface by a bombardment with slow electrons. For mica

the same limit was found at 2600 Å., corresponding to 4.8 volts.

If the activated crystal is not illuminated with visible light, we assume neutral sodium atoms with a very low ionization energy to exist in the crystal. Light of 8000 Å. is still able to produce electronic conductivity inside such crystals. We conclude, therefore, that the ionization potential of sodium in rock salt is 1.5 volts or less. It may be that infra-red light of still longer wave lengths does not ionize only because it is not absorbed, while the energy quantum $h\nu$ in such light may suffice for the purpose.

We may further suspect that a higher frequency is required for the photoelectric effect when the activated crystal is not exposed to visible light. The effect corresponds in this case to a removal of electrons from neutral sodium atoms. In fact, a wave-length limit of 2600 Å., corresponding to 4.76 volts was found in this case. The energy is larger by 0.9 volts than for free electrons. This must be the ionization potential of the free sodium aggregates in the crystal.

In the following table the data for rock salt are given in wave lengths and in volts.

	ν	V
Energy of an ion.....		7.9
Conductivity (ionization of Cl^- inside the lattice)	$>1500 \text{ \AA.}$ ($<2800 \text{ \AA.}$)	<8.3 (>4.4)
Photoelectric effect (removal of Cl^- electrons from the lattice).....	2000 Å.	6.2
Photoelectric effect on activated crystals (removal of Na electrons from the lattice).....	2600 Å.	4.76
Photoelectric effect on activated crystals exposed to visible light (removal of free electrons from the lattice).....	3200 Å.	3.9
Photoelectric effect on rock salt with an electronic deposit on the surface (removal of electrons from the surface).....	3100 Å.	4.0
Conductivity of activated crystals (ionization of Na inside the lattice).....	$>7000 \text{ \AA.}$ ($<8000 \text{ \AA.}$)	<1.76 (>1.5)

The problem of the energy of an electron in the dielectric and of the conditions for its removal may also be attacked in another way, to wit, by pushing the electrons into the dielectric from a metal. It requires a study of the photoelectric effect on the boundary between the metal and the dielectric. Such experiments, both on large surfaces and on colloidal particles, are now in progress, but as yet have not given definite quantitative results. A bombardment of the dielectric by electrons of increasing velocities may give valuable information about the ionizing potentials of different electrons in a crystal lattice.

The possibility of having in the same crystal either electrons or ions may be of great importance in the study of the problem of the equilibrium contact potential, and presumably also for the problem of frictional electricity. All those problems require more experimental work, however, which is at present in progress.

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LECTURE XIV

THE PROBLEM OF DIELECTRIC LOSSES

While the problem of the conductivity of dielectrics and the validity of Ohm's law for these bodies produced an extensive literature and was regarded from many divergent points of view, this is still truer of the problem of the heat developed by the current and the validity of Joule's law of heating. The heat problem became of high practical importance through the use of dielectrics in alternating fields, especially where high frequencies were used. Many hundreds of papers are devoted to this problem. They agree in the statement that Joule's law in the form

$$W = \int_0^T \frac{V^2}{R} dt, \quad (69)$$

does not, in general, represent the heat actually developed in alternating fields, the observed heat being often thousands of times less than anticipated. The heat energy actually observed and lost by a dielectric in an alternating electric field is an involved function of frequency, temperature, and electric field, which apparently cannot be represented by equation (69). Furthermore, the experimental results obtained on different dielectrics are often contradictory with regard to the influence of the above factors and none of the several explanations proposed has succeeded in giving a complete account of the observed phenomena.

The knowledge of the mechanism and the laws of the electric current in dielectrics, which have been developed in these lectures seems, however, to furnish an adequate explanation of dielectric losses, without any new hypotheses. Thus we shall find that equation (69), representing Joule's law, gives the true heat if properly applied and interpreted.

The denial of the validity of this law given in all electro-technical papers is due in the first place to the use of a wrong value for the resistance R ascribed to the dielectric. The resistance used is usually measured either by direct current or by a current of low frequency on the basis of the relation

$$R = \frac{V}{I}. \quad (70)$$

We know, however, that the current I sometimes decreases very rapidly after the application of the potential and this decrease is due to the opposing electromotive force P , produced by polarization due to space charges. Usually the current I is measured at a time when the maximum of P is reached. This final current I_f may be represented by the equation

$$I_f = \frac{V - P_m}{R}.$$

and the real resistance of the dielectric is given by:

$$R = \frac{V - P_m}{I_f}. \quad (71)$$

It is clear that in using equation (70) instead of the correct equation (71), an error is involved, which depends upon the ratio P_m/V .

A second error is introduced by neglecting the space charges and electromotive force P produced by the alternating field.

By correcting these errors we can obtain a satisfactory theory of dielectric losses considered as the heat developed by the current according to Joule's law. The usual representation of a dielectric consists of a capacity C with a resistance R shunted across it (Fig. 47). The phenomenon of space charges requires that we introduce a supplementary modification of this scheme. Dielectrics, like calcite, are adequately represented in their behavior by the schematic figure (Fig. 48). Here C denotes the geometric capacity of the dielectric; R its resistance; C_1 the capacity of the polarized layer, where the space charges are accumulated; and R_1 the resistance of this layer.

Dielectrics with a diffuse distribution of charges may still be represented by Fig. 48, with the difference that C_1 is of the same order of magnitude as C , while it is much greater for calcite. In calcite the resistance R_1 is very large relative to R , while for a diffuse distribution this ratio is not so large.

A complication may occur if the conductivity of the whole crystal is changed by the transfer of ions and by the resulting change in the conditions for the dissociation equilibrium, as was found to be the case in quartz. In some cases, stationary heterogeneity in the dielectric may occur as a result of the transfer of ions. As in the practical problems

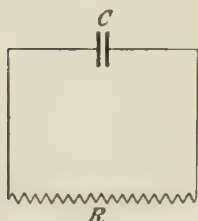


FIG. 47.

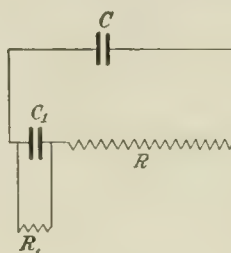


FIG. 48.

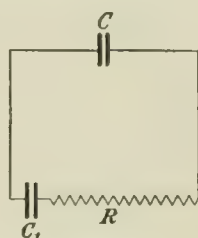


FIG. 49.

of dielectric losses, we are interested in stationary conditions maintained by an indefinite number of cycles of the alternating field, the final conductivity of the changed dielectric must be used for calculations.

For many dielectrics used in industry, we may simplify the scheme given in Fig. 48 by neglecting the conductivity of the polarized layer, and considering the space-charge condenser C_1 as an ideal insulator. Thus we obtain the simplified scheme (Fig. 49).

We can now develop the theory of dielectric losses for insulators that are characterized by Fig. 49. We notice that for such a dielectric the superposition law holds. This law was represented by the equation (8), which we will write in the form

$$I_t = \frac{1}{R} \int_0^t \frac{dV}{d\tau} \varphi(t - \tau) d\tau. \quad (72)$$

We now assume, as is usually done for an alternating current, that

$$V = V_o \sin \omega t, \quad (73)$$

and corresponding to equation (53),

$$\varphi(t) = e^{-\frac{t}{C_1 R}}. \quad (74)$$

Equation (72) then gives, after the proper trigonometric operations,

$$I_t = \frac{V_o}{R} \frac{\omega^2}{\omega^2 + \frac{1}{R^2 C_1^2}} \sin \omega t + \omega V_o \frac{C_1}{1 + C_1^2 \omega^2 R^2} \cos \omega t. \quad (75)$$

To the conduction current I_t we must now add the displacement current

$$I_d = C \frac{dV}{dt} = C \omega V_o \cos \omega t. \quad (76)$$

The total current I in the dielectric is then equal to:

$$I = I_t + I_d = \frac{V_o}{R} \frac{\omega^2}{\omega^2 + \frac{1}{R^2 C_1^2}} \sin \omega t + \omega V_o \left(C + \frac{C_1}{1 + C_1^2 \omega^2 R^2} \right) \cos \omega t. \quad (77)$$

The first term in the equation represents the current which is in phase with the potential difference V given by equation (73), while the second term has a phase differing by $\pi/2$. The average energy loss during one full period is therefore given by the first term only, and is equal to:

$$W = \frac{V_o^2}{2R} \left(\frac{\omega^2 R^2}{\omega^2 R^2 + \frac{1}{C_1^2}} \right). \quad (78)$$

Instead of the energy loss W , it is often easier to measure the phase difference δ between the actual current I and the current which would be drawn by a perfect condenser. This angle of loss is given by:

$$\tan \delta = \frac{\omega R}{C} \left(\frac{C_1^2}{C_1^2 \omega^2 R^2 + 1 + \frac{C_1}{C}} \right), \quad (79)$$

according to equation (77).

The first factors in equations (78) and (79) give the value, following from the usual representation of a dielectric by a capacity C and constant resistance R (Fig. 47). The second factors represent the correction caused by the use of the condenser C_1 , representing the space charges of polarization. We shall test equations (77), (78), and (79) with the extended experimental material collected by electrotechnical investigations.

It was found that the dielectric constant depends on the frequency increasing when the frequency of the alternating field used for measurement decreases. We must remember, however, that the calculation of the dielectric constant is usually based on the picture of a dielectric as consisting of a condenser corresponding to the Fig. 47, instead of Fig. 49. The current I is thus usually represented by the equation

$$I = \frac{V_o}{R} \sin \omega t + \omega V_o \cdot C \cdot \cos \omega t. \quad (80)$$

Using equation (80) instead of equation (77) and measuring the capacity by the coefficient of the second term, we obviously obtain in place of C a quantity

$$C' = C + \frac{C_1}{1 + C_1^2 \omega^2 R^2}, \quad (81)$$

which shows the observed dependence on frequency and temperature.

The experimental data therefore does not actually force us to assume a *real* dependence of the dielectric constant upon the frequency, as was believed. *We are accordingly led to consider the real dielectric constant of crystals as independent of frequency.*

The dependence of the dielectric losses on frequency is given by equations (78) and (79). Plotting $\tan \delta$ against ω we find a curve like that represented in Fig. 50. The ω_m corresponding to the maximum of $\tan \delta$ is given by the equation:

$$\begin{aligned} \frac{d \tan \delta}{d \omega} &= 0, \\ \omega_m &= \frac{1}{C_1 R} \sqrt{1 + \frac{C_1}{C}}. \end{aligned} \quad (82)$$

The experimental material in the past seemed in spots to be contradictory, as some of the measurements showed an increase of $\tan \delta$ with frequency, while others gave a decrease of the angle of loss with frequency. In some other cases, a frequency producing a maximum angle δ was found in the region of audible frequencies. This, it is seen, follows from the above relations. Hence, as far as data for the corresponding dielectric could be found or measured, a satisfactory agreement with the present theory was found in all cases.

The most accurate measurements with a complete set of data characterizing the composition of the dielectric

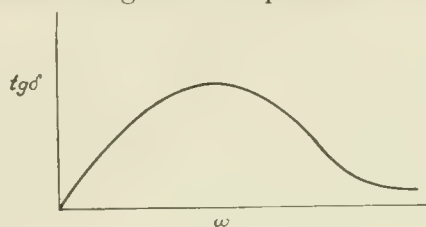


FIG. 50.

used were published by Schott on glass. Sinelnikov and Walther prepared and tested a glass of the same chemical composition as given by Schott for glass 015. They measured C , R , and C_1 and on the basis of these data computed the angle of loss at a frequency of 10^6 cycles. While Schott found $\delta = 6.67'$, the computation gave $\delta = 6.9'$.

Another test was made on a condenser of paper impregnated with paraffin. The angle of loss was found for the frequency 314 to be $\delta = 5.4'$, while the measured values of C_1 , R_1 , and C led to a value $\delta = 5.9'$. At a frequency of 3,140 the measured value of δ was $48.1'$ and the computed $47.0'$. Thus, not only is the dependence on frequency, but also the absolute value found to be in a sufficiently close agreement with experiment, which shows that using equations (78) and (79), we obtain the right magnitude of the dielectric losses. Those equations are, however, the expression of Joule's law applied to the scheme of a dielectric shown in Fig. 49.

Equations (78) and (79) may be used in a different way. Measuring $\tan \delta$ or W for two frequencies and knowing C as given by the dielectric constant and geometrical dimensions, we may compute R and C_1 and thus find the losses at any frequency.

The dependence of dielectric losses on temperature is given by the variation of the resistance R with temperature. From the usual picture of a dielectric (Fig. 47), leading to equation (80), a continuous increase of losses with temperature is to be expected, because of the decrease of the resistance R according to the equation:

$$R = R_0 e^{\frac{\alpha}{T}}. \quad (83)$$

Experiment did not confirm this conclusion in general. For many dielectrics the losses at first increase with rising temperature, then reach a maximum and decrease. For others they increase once again at higher temperatures.

In order to consider losses resulting from equation (78) we may write it in the form:

$$W = \frac{V_o^2}{2} \cdot \frac{1}{R} \cdot \frac{1}{1 + \frac{1}{C_1^2 \omega^2 R^2}}. \quad (78^a)$$

We then distinguish two extreme cases: (1) $C_1^2 \omega^2 R^2$ is very large relative to unity; and (2) $C_1^2 \omega^2 R^2$ is very small. In the first case we may neglect the second term $1/C_1^2 \omega^2 R^2$ in the denominator. Equation (78^a) then reduces to $V_o^2/2R$ as in the usual equation (80) and requires an increase of losses with temperature. In the second case, we may neglect 1 against $1/C_1^2 \omega^2 R^2$ and equation (78^a) gives $\frac{V_o^2}{2} \times C_1^2 \omega^2 R$. The losses will in this case obviously decrease with temperature. The first case corresponds to low temperatures, where

$$R^2 > \frac{1}{C_1^2 \omega^2}. \quad (84)$$

The second case takes place at higher temperatures.

On increasing the temperature we might, therefore, expect first an increase and then a decrease with some maximum between.

The schematic representation of Fig. 44 and equations (78) and (79) resulting from this scheme are sufficient for a qualitative, and often even for a quantitative, description of dielectric losses. Using this theory we must, however, remember that it is limited by the condition that the conductivity of the polarized layer may be neglected and that no current is supposed to flow through this layer. This condition is chiefly fulfilled at low temperatures; for many technical insulators it holds at room temperature. With increasing temperature the ratio of the maximum electromotive force of polarization P_m to the applied potential V becomes smaller. This means that the ratio of the final current I_f to the initial current I_o increases, as shown in the diagram of Fig. 31, and the ratio R_1/R decreases. The conditions underlying the simplified equations (78) and (79) may be formulated in the following terms:

$$\frac{R_1}{R} = \infty; \frac{P_{\max}}{V} = 1; \frac{I_f}{I_o} = 0, \quad (85)$$

These conditions do not hold for high temperatures, until we reach a second limiting case of very high temperatures characterized by:

$$\frac{R_1}{R} = 1; \frac{P_{\max}}{V} = 0; \frac{I_f}{I_o} = 1. \quad (86)$$

The latter conditions are equivalent to the usual picture of a body characterized by the dielectric constant and a constant and uniform specific resistance (Fig. 47).

Between the limits of validity of equations (85) and (86) we must use the more complicated but accurate representation (Fig. 48). Contrary to the two limiting cases, the superposition law does not hold for the case of Fig. 48. Moreover, the resistance R_1 is not constant and the equations are not linear. To a sufficient approximation we may set R_1/R proportional to P . The more accurate formula may then be obtained from equations (41), (43), and (45).

The density of the mobile negative ions is proportional to the conductivity. In the normal crystal $n_- = n_+$. In the polarized layer:

$$\frac{n_-}{n_+} = 1 - \frac{\epsilon \cdot \alpha^2}{4\pi e n_+} \cdot V_o e^{-\alpha x}. \quad (87)$$

V_o is equal to the polarization P , and the ratio n_-/n_+ may be found from $n_-/n_+ = R/R_1$. We thus obtain

$$\frac{R}{R_1} = 1 - \frac{\epsilon \alpha^2}{4\pi e n_+} e^{-\alpha x} \cdot P. \quad (88)$$

The use of the complete scheme of Fig. 48 does not involve essential difficulties. Practical numerical results can be always obtained. The dependence of dielectric

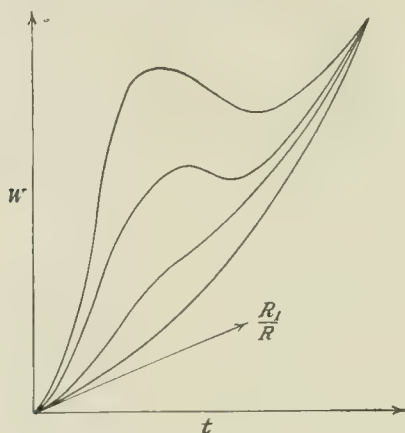


FIG. 51.

losses upon the temperature may be represented for different ratios R_1/R by Fig. 51.

In strong alternating electric fields the dielectric losses were found to be a function of the electric field E represented by the equation:

$$\log W = a + CE. \quad (89)$$

This equation is also sufficiently explained by our theory. In fact, we shall find in one of the following lectures (Lecture XVI), that the resistance of the polarized layer R_1 decreases when P exceeds 2,000 volts and gradually falls

with increasing P . Thus we will find the same law as that of equation (89) for the conductivity of the polarized layer, and accordingly also approximately for W . The distribution of potential for this case is represented in Fig. 34.

We must therefore conclude that *a theory explaining the dielectric losses by Joule's heat gives an adequate account of all the experimental results* if the actually observed mechanism of conductivity is properly taken into account. By this statement we do not deny the existence of some supplementary losses of different origin, such as those involving the orientation of molecules in a viscous liquid, the Maxwellian effect of heterogeneous dielectric constants, etc.

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LECTURE XV

BREAKDOWN OF DIELECTRICS BY HEAT

The electrical theory of crystal lattices should enable one to calculate the electrical field which would be able to destroy the crystal by pulling out the ions from their equilibrium positions. The dielectric strength computed in this way leads to values of the field of over 10^8 volts/cm., while the breakdown actually observed occurs at about $2 \times 10^5 - 8 \times 10^5$ volts/cm. The observed dielectric strength is thus about two hundred times less than the expected value, just as in the case of the mechanical strength.

Several explanations were proposed for the breakdown of dielectrics in strong fields. Up to within the last 2 years none of them had a proper experimental basis and quantitative proof. The best-known theory, developed by K. Wagner, explains the breakdown by a local heating effect. Wagner emphasizes the influence of weak spots possessing higher electrical conductivity than the average. Joule's heat developed in those spots raises the temperature, which increases the conductivity still more. This leads to a higher heat production, and so on. If the amount of heat removed by heat conduction from the weak spot be less than the heat developed by the current, the temperature will rise continuously and reach the melting point, or even the boiling point, which will obviously result in a puncture of the dielectric.

The weak spots, however, are not essential for Wagner's theory. The same mechanism may be responsible for the breakdown of a completely homogeneous dielectric. Alexander Walther and Miss Inge furnished an experimental basis for the theory by an extended investigation of rock salt and glass. The theory was simultaneously worked out by Semenoff, Walther, and Fock in Leningrad, and by

Rogovsky and V. Karman in Aachen. A uniform heating of the dielectric, leading to a breakdown, was also directly shown by Semenoff and Walther. Applying gradually increasing potential differences to a plate of rock salt maintained at 500°C . (a little below the temperature of incandescence) they were able to follow the rise of temperature and its distribution by the red light emitted by the plate. They ascertained that the temperature was highest in the middle, rose with increasing potential and at that point reached the melting point. At those places a channel of partly molten and partly evaporated salt was observed whose appearance was that usually observed in this type of heat breakdown. A rough idea of the conditions leading to a breakdown by heat may be given in the following way. If the dielectric does not break down continuously, it means that some equilibrium temperature t is reached such that the amount of heat developed is equal to the heat transferred by conduction. Let us consider a plate of the thickness D with a very large area. We thus may neglect the heat flow in the plane of the plate. The heat Q_1 developed in a cylinder of 1 cm.^2 cross-section will be

$$Q_1 = \frac{V^2}{\rho D}, \quad (90)$$

where Q_1 is expressed in joules, V denotes the potential difference, and ρ the specific resistance which may be approximately represented by

$$\rho = \rho_0 e^{-\alpha t}. \quad (91)$$

On the other hand, we put the heat Q_2 transferred by heat conduction proportional to the temperature difference between the crystal and the electrodes as

$$Q_2 = \frac{K(t-t_0)}{D}. \quad (92)$$

At equilibrium temperature

$$Q_1 = Q_2. \quad (93)$$

In order to assure the stability of the equilibrium, we must, furthermore, require:

$$\frac{dQ_1}{dt} \leq \frac{dQ_2}{dt}. \quad (94)$$

Figure 52 represents the value Q_1 as function of t for several applied potentials V . The straight line gives Q_2 for some temperature t_0 of the electrodes. We see directly that for curve 1, corresponding to the potentials V_1 , some equilibrium represented by the crossing point A of the curves for Q_1 and Q_2 is easily found. No equilibrium can exist for potentials corresponding to curve 3. The highest

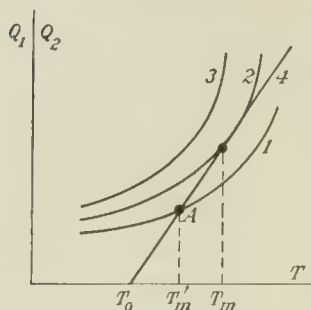


FIG. 52.

possible potential V_c allowing an equilibrium according to curve 2 is given by the condition

$$\frac{dQ_1}{dt} = \frac{dQ_2}{dt}. \quad (95)$$

The potential V_c represents, therefore, the breakdown potential of the dielectric plate. Equations (90), (92), (93), and (95) give

$$\left(\frac{V_c}{D}\right)^2 = C \frac{\rho_0 e^{-at}}{a}. \quad (96)$$

In order to obtain a more accurate equation for V_c we must consider that the temperature t and, therefore, the resistance ρ cannot be uniform throughout the channel considered and that t cannot exceed the melting point. Equation (92) for the heat conduction must be replaced by the usual expression for heat conductivity. For an infinitesimal volume at a distance x from the surface of the plate the equilibrium condition will be:

$$\left(\frac{V}{\int \rho dx}\right)^2 \cdot \rho - k \frac{d^2 t}{dx^2} = 0, \quad (97)$$

where ρ may again be represented by equation (91). For the conditions at the boundaries we must consider the flow of heat to and through the electrodes. Semenoff and Fock found for V_c the expression:

$$\left(\frac{V_c}{D}\right)^2 = \frac{33.6 \cdot k \cdot \rho_0}{a} e^{at_0} \cdot e^{-f(a)}, \quad (98)$$

where $f(a)$ is a function depending on the ratios of the thickness and heat conductivity of the dielectric and electrodes.

Assuming the exact expression for ρ , namely

$$\rho = \rho_0 e^{\frac{\alpha}{T}}, \quad (99)$$

Walther and Inge found:

$$\left(\frac{V_c}{D}\right)^2 = \frac{8k\rho_0}{\alpha} T_0^2 e^{\frac{\alpha}{T}} \left(1 + \frac{2T_0}{\alpha\beta} + \dots\right). \quad (100)$$

Equation (98) leads to a dependence of the breakdown potential on the temperature t given by:

$$\frac{\partial(\log V_c)}{\partial t_0} = -\frac{a}{2}. \quad (101)$$

Equation (100) gives:

$$\frac{\partial(\log V_c)}{\partial(1/T_0)} = \frac{\alpha}{2} - T_0. \quad (102)$$

The resistance of rock salt between 400°C. and the melting point is best represented by equation (91). The

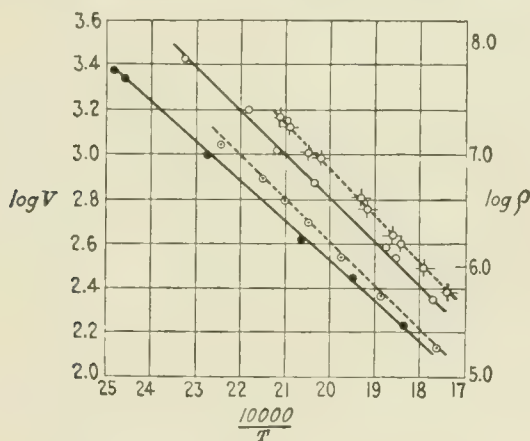


FIG. 53.

resulting equation (98) for V_c was checked by experiments with the accuracy to be expected from the magnitude of the experimental errors.

The more general equation (100) was checked by the experiments of Walther and Inge on several kinds of glass. Figure 53 gives the measured data for two sorts of glass. The heavy lines represent $\log (V_c^2)$, the dotted ones the log of the resistance ρ . Both are straight. The slope is,

according to equation (102), greater for ρ and the difference was found close to the predicted value $2T_o$. This difference is small, as α is about 10^4 for all dielectrics, while $2T_o$ is only about 600. Equation (100) gives:

$$\frac{1}{\rho} \left(\frac{V_c}{D} \right)^2 = \frac{8k}{\alpha} T_o^2 \left(1 + \frac{2T_o}{\alpha} + \dots \right). \quad (103)$$

This ratio must be independent of the resistance and thus the same for all sorts of glass to the extent to which we may regard the heat conductivity K and α as equal. In Fig. 53 we find, in fact, that $\log (V_c^2) - \log \rho$ is equal for both glasses.

Using different electrodes, Semenoff, Walther, and Inge found that the dependence of V_c on the heat conductivity,

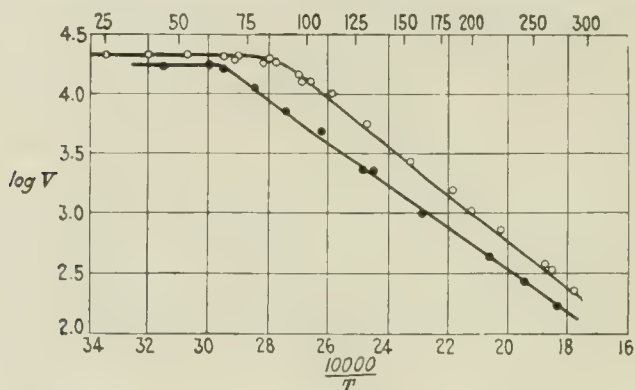


FIG. 54.

the size of the electrodes, and the dielectric plate agreed well with the calculated value of $f(a)$ in equation (98).

The absolute value of V_c calculated on the basis of equations (98) or (100) agrees with the measurements quite satisfactorily. It is especially important that on approaching the melting point the breakdown potential drops to the very small values of 50 to 100 volts, which are obviously due to a melting by the current. Those small values rise continuously and regularly at lower temperatures to the usually observed high potentials. Figure 54 gives the breakdown potentials for two sorts of glass as a function of temperature. Similar curves were obtained for rock salt.

In these curves we see two domains sharply separated. From the melting point down to some temperature (about 100° for glass and about 150° for rock salt), the breakdown potential rises exponentially. Starting from this temperature and down to the liquid air temperature V_c remains constant, independent of temperature.

According to the considerations above, the influence of the temperature upon the breakdown potential represented in the Fig. 53 and the high-temperature part of Fig. 54 is the essential feature of the heat theory of breakdown. If this peculiar property disappears we must deny the heat explanation and look for another one.

In fact, several phenomena indicate an entirely different mechanism of breakdown for low temperatures.

While the position at which puncture occurs at high temperature is usually given by location of the point where the cooling is least, *i.e.*, chiefly near the center of the electrodes, at low temperatures the puncture usually takes place at the edge of the electrode where the field is highest.

While the rupture at high temperatures requires some measurable time to develop the heat, it occurs instantaneously at low temperatures.

While the heat conductivity of the electrodes has a distinct influence upon the breakdown at high temperatures, it is of no influence at low temperatures. Nor has the shape of the crystal any influence as long as the field is the same.

While the comparatively good electrical conductivity requires a short time to produce breakdown at high temperatures, we could easily compute that for the most dielectrics many hours would be necessary to heat it by the current to a high temperature even if we neglect the heat conductivity completely. We thus conclude that the mechanism responsible for breakdown at room temperature must be different from Joule's heat. The electric field only limits the potential. Taking into account the space charges and correcting the field for these, we found, as condition for breakdown at low temperatures, a definite

electric field E which varied for different dielectrics between $2 \cdot 10^5$ volts per centimeter and $8 \cdot 10^5$ volts per centimeter.

There are, however, some exceptions to this rule. In crystals of the calcite type we noticed a concentration of the field in a thin polarized layer of the thickness of 10^{-4} cm., while the drop of potential was over 1,000 volts. Thus an average field of over 10^7 volts per centimeter exists in those layers. In trying to find the limit for this field we found that as soon as the potential exceeds a few thousands of volts the thickness of the sheet begins to increase so that the field never exceeds $(2.5) \times 10^7$ volts per centimeter. In the case of calcite, the thickness of the polarized layer is given by the equilibrium of ions and cannot be artificially changed. We are able, however, to produce in dielectrics like glass, quartz, or mica thin non-conducting sheets of a desirable thickness by removing at high temperature the mobile ions from a sheet adjacent to the anode. We found for such dielectrics subjected previously to the described process of formation that the drop of potential never exceeded a value of a few thousands of volts. For a higher applied potential difference we got the potential distribution shown on Fig. 43. This indicates that the *conductivity* of this formed non-conducting layer begins to increase above potential differences of the order of 5,000 volts. The potential at which the increased conductivity occurs is the same no matter what the thickness of the non-conducting layer may be.

One may then well ask what the cause of the exceptionally high fields observed in the naturally polarized or artificially formed layers may be. We might at first try to hold the small conductivity of those layers responsible for their dielectric strength. We ascertained, however, that using materials of different origin (American calcite or fused quartz) with a uniform conductivity lower than that reached in those layers, we got the same breakdown fields of about 5×10^5 volts per centimeter instead of the 5×10^7 volts per centimeter observed in the polarized layers. Thus the low conductivity is not the cause of this phenom-

enon. It is therefore essential that the layers withstanding high fields be very thin. The presence of the remaining thick portion of the crystal with the small potential gradient is of no influence. In fact, by using very thin sheets of glass and mica we were able to produce even there the same high fields of over 10^7 volts per centimeter.

We thus conclude that the limit of several hundred thousand volts per centimeter for the field holds for thick sheets of the dielectrics only. It fails absolutely for very thin sheets. The importance influence of the thickness indicates a cumulative process going on through the thickness, as, for instance, an accumulation of ions when ionization by impact takes place. The influence of the thickness is just as characteristic for the new type of breakdown, that is, the ionization by collision, as the influence of temperature is for the heat production. We shall now show that the ionization hypothesis is actually justified by the experimental investigation.

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LECTURE XVI

BREAKDOWN BY IONIZATION

We shall consider N_0 ions starting from one electrode and assume that after some distance d travelled in the electric field E_c they become able to produce N_0 new ions. In this distance the number of ions is doubled. In the distance $2d$ the number of ions becomes equal to $4N_0$, etc. If the thickness of the dielectric between the electrodes be D , the number of ionizations for each ion on its way through the dielectric will be

$$z = \frac{D}{d},$$

and the number of ions produced

$$N = N_0 2^{\frac{D}{d}}. \quad (104)$$

The distance d cannot exceed the distance where the ion reaches its final uniform velocity v_0 which is proportional to the electric field E . The validity of Ohm's law even for high fields and small thicknesses indicates that d must be very small. If so, $z = D/d$ must usually be a large number and the number of ions N produced by ionization so large that breakdown may be expected immediately after the ionization begins. In fact, if we take for d a value 10^{-4} cm., which is surely far too high then for $D = 1$ mm., we obtain

$$\frac{N}{N_0} = 2^{1,000} = 10^{300}.$$

There is no doubt that an increase of the number of mobile ions of such a magnitude must result in a distortion of the dielectric.

Obviously, a breakdown becomes inevitable as soon as the field E_c producing cumulative ionization is reached, independent of the particular value of D or d , if D is large.

If, however, D/d is a comparatively small number (*i.e.*, about 5 or 10), the conclusion expressed above is no longer correct. The number of the ions may increase a few hundred times, which will result in an increase of the current, say from 10^{-10} to 10^{-8} amp. There will be, however, no reason for a breakdown. We shall make the hypothesis that the condition for a breakdown in such a case is reached as soon as the density of ions in the dielectric exceeds some limiting value n_c . It may be that the increased conductivity then leads to a puncture by the same heat mechanism as described above. Whatever the last step may be it seems probable that the first step in determining whether or not breakdown occurs is the density n_c of mobile ions.

We shall now formulate the results of our assumption by calculating the number of ions produced in a dielectric when a field E exceeding the field producing ionization is applied. We may reasonably suppose that the ion must fall through some potential difference P in the field E in order to produce ionization. The distance between two ionizations produced by the same ion will be P/E . The probability of an ion knocking out a new ion in a distance

dx is $\frac{E}{P} dx$. If N ions pass at a distance x from one electrode through a cm.², the number passing in the distance $x + dx$ will be larger by $dN = N \frac{E}{P} dx$. The

number of ions N_0 starting at a distance x_0 will increase to a value

$$N = N_0 e^{\frac{E}{P}(x - x_0)}$$

at the distance x .

In order to get the total number of ions reaching the opposite electrode at the distance D , we shall put $x = D$ and consider ions starting from all distances from $x_0 = 0$ to $x_0 = D$; the number of initial ions starting from a slice

dx_o will be $n_o dx_o$, where n_o denotes the normal density of ions in a cm.³. We then obtain for N

$$N = n_o \int_0^D e^{P(D-x_o)} dx_o = n_o \frac{P}{E} (e^{E_D} - 1). \quad (105)$$

The average density of ions n takes on the value

$$n = \frac{N}{D} = n_o \frac{P}{ED} (e^{ED} - 1) = n_o \frac{P}{V} (e^{\frac{V}{P}} - 1). \quad (106)$$

We may complete equation (106) by expressing the normal density of ions as a function of temperature T ,

$$n_o = \nu_o e^{-\frac{\alpha}{T}}, \quad (107)$$

where $\alpha = U/K$, U being the ionization energy of the ion, K the Boltzmann constant, and ν_o the total number of those ions in a cm.³. We thus obtain

$$n = \nu_o e^{-\frac{\alpha}{T}} \times \frac{P}{V} (e^{\frac{V}{P}} - 1). \quad (108)$$

Or approximately for large V/P , even if $V/P > 3$,

$$\log n = \log \nu_o - \frac{\alpha}{T} + \frac{V}{P} - \log \frac{V}{P}. \quad (109)$$

The condition for a breakdown according to our hypothesis is a definite value of n or $\log n$. If we could regard P as constant independent, both of field and temperature, the condition for a breakdown would be

$$\frac{V}{P} - \frac{\alpha}{T} = \text{constant}, \quad (110)$$

with P and α constant. We may, however, expect P to be a function of the field. Assume that an ionization energy P_o must be accumulated by the ion to knock out a new ion on impact. We must assume that, before this energy is reached, the ion loses some of the energy given it by the field due to impacts on its way. The lower the field, the longer the path traversed before P_o is reached and the greater the loss of energy by impacts. Obviously, the potential difference P between two ionizing collisions of the same ion must be larger when the field is weaker than when it is stronger, even though P_o is constant.

The distance d between two ionizing collisions is many hundreds of times greater than the atomic distances. Hence the ion must be subjected to a great number of collisions on its way. It is justifiable, therefore, to apply statistical methods assuming as usual that the resistance of the lattice is proportional to the velocity u of the ion. For the terminal velocity u_o below the field necessary for ionization we have, according to Ohm's law,

$$u_o = vE, \quad (111)$$

where v denotes the mobility of the ion.

The equation for the velocity of the ion is then

$$m \frac{du}{dt} = eE - \frac{eu}{v}, \quad (112)$$

$$u = vE \left(1 - e^{-\frac{e}{vm}t} \right). \quad (113)$$

The distance x passed over by the ion in a time t is

$$x = \int_0^t u dt = vE \left[t - \frac{vm}{e} \left(1 - e^{-\frac{e}{vm}t} \right) \right]. \quad (114)$$

The relation between u and x is

$$\frac{du}{dx} = \frac{du}{dt} \cdot \frac{dt}{dx} = \frac{\frac{eE}{m} - \frac{eu}{vm}}{u} = \frac{eE}{m} \left(\frac{1}{u} - \frac{1}{vE} \right). \quad (115)$$

Or, in integral form,

$$u + vE \log \left(1 - \frac{u}{vE} \right) = - \frac{e}{vm} x; \quad (116)$$

for small u/vE , when the friction may be neglected, we obviously have:

$$\frac{u^2}{2} = \frac{eE}{m} x. \quad (117)$$

Below the ionization limit the time t_o necessary to reach the maximum velocity is independent of the field. The distance x traveled before this velocity is reached is proportional to the field E . It is highest at the breakdown field E_c . If the final kinetic energy of the ion

$$\frac{1}{2} m u_o^2 \geq eP_o, \quad (118)$$

we assume that ionization occurs as soon as the energy P_o , is reached. This energy is then lost by the ion and a

new accumulation of energy begins. The time λ spent to reach the energy P_o is less than λ_o as shown in Fig. 55, in which the velocity of the ions is plotted against time for different potentials. The potential P represents the potential needed to give the critical ionizing velocity u_c . For higher fields it is less and thus it is obvious that the average velocity of the ions diminishes slowly as the field increases. For very high fields the average velocity \bar{u} approaches one-half of the maximum velocity u_c of ions just at the breakdown field. The time between ionizing collisions λ becomes shorter and diminishes more rapidly than

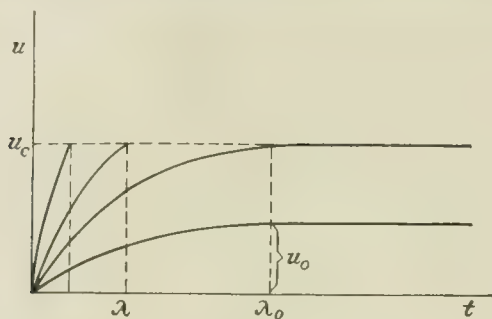


FIG. 55.

inversely proportional to the field, so that the distance between two collisions $d = u\lambda$ decreases more rapidly than inversely proportional to E . Therefore, the potential difference P between two collisions $P = Ed$ decreases when the field increases, and

$$P = P_o + \frac{A}{E^n}. \quad (119)$$

There is no evidence that P or P_o depends to any considerable extent upon temperature.

In our considerations we used the picture of a uniform field E in the dielectric. It is obvious, however, that if ions of one sign only are mobile and ionizing, every layer of the dielectric loses the ions which were produced in that layer and removed by the field. As the number of ions increases from $x = 0$ to $x = D$ in the direction in which

they move, more ions are removed from each volume than come in. As a result, a space charge through the whole dielectric must appear and disturb the potential distribution. In a stationary state the current through the dielectric must be constant and therefore the potential gradient inversely proportional to the density of mobile ions. The gradient will be highest about the electrode at which the ions start and lowest at the point where they arrive. Were P independent of field the potential distribution could not change the number of ionizations V/P and the number of ions produced. As P decreases with increasing field the number of ions will depend not only on the total potential difference V but on the distribution. The number of ions produced will generally increase when the field ceases to be uniform. The number of collisions, however, can never exceed V/P_0 .

Having discussed the picture arising from the hypothesis of a cumulative ionization by collision, we shall now compare it with experiment. The picture must be tested for a small number of ionizations V/P only. From equation (106) we may conclude that for $V/P = 10$, the density of ions n increases about 2,000 times, which usually does not lead to breakdown. For $V/P = 20$, n increases about 2.5×10^7 times and produces a breakdown. In order to test the theory we must, therefore, use dielectrics of a thickness less than ten to twenty times the maximum distance d , in which the final velocity of the ion is reached. If d is of the order of magnitude of 10^{-5} cm. the thickness of the dielectrics investigated ought to be about 10^{-4} cm. K. Sinelnikov and T. Kurchatov carried out this investigation on thin foils of glass obtained by blowing, on thin sheets of split mica, on solidified sheets of colophonium and wax, and on thin sheets of oil and benzol.

They found that while the breakdown potential V_c increased in thick sheets of a dielectric in direct proportion to the thickness, such that the breakdown field $E_c = V_c/D$ remains constant, this condition no longer holds for dielectrics of a thickness less than 5×10^{-4} cm. or 5μ . From

5μ down to 0.2μ the potential V_c remains almost constant, while the field E_c increases as shown in Figs. 56 and 57. In Fig. 56 the field E_c is plotted against the thickness D ; in Fig. 57 $\log E_c$ is plotted against $\log D$. Both diagrams represent the data for glass.

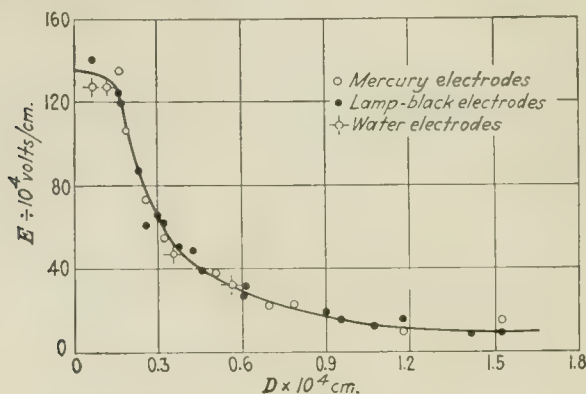


FIG. 56.

The shape of the curves is in very satisfactory agreement with the theory developed. The results were independent of the nature of the electrodes, as may be concluded from

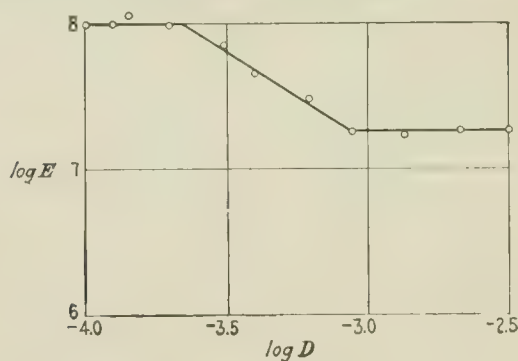


FIG. 57.

Fig. 56, where electrodes of mercury, lampblack, and water gave identical breakdown fields. Figure 57 is especially illustrative. It shows the relative values of D and E on an equal scale and therefore gives an adequate uniform picture over the whole range of thicknesses and

fields used. The breakdown field E_c which has for sheets $D > 5\mu$ a value of about 5×10^5 volts per centimeter increases for a thickness of 0.2μ to 10^8 volts per centimeter.

The influence of temperature on the breakdown of thick sheets was negligible. Below the limit of 5μ an increase of temperature decreased the breakdown field in such a manner that thinner sheets were necessary to stand the same electric field. The relation (110) was quantitatively satisfied for 15, 50, and 100°C ., assuming for α the value 10^4 and assuming P independent of temperature.

We next proceeded to a direct proof of the assumption that the number of ions increases in a cumulative manner if the field exceeds the ionization limit. The number n of ions could be measured by the current I flowing through the dielectric according to the relation

$$I = n \cdot e \cdot v \cdot E, \quad (120)$$

$$\frac{I}{E} = e \cdot v \cdot n.$$

In using this relation between the number of ions and the current, we assume that the mobility v may be regarded as constant. We know that this assumption cannot be accurate, as was shown on the basis of Fig. 55, for the average velocity decreases at the same time that the field increases; that is, in fields producing ionization by impact the mobility of the ions is not independent of the field, but decreases even more rapidly than inversely proportional to the field. For purposes of discussion, however, the approximation may be allowed. Another question that may be raised is as to whether the type of friction represented by the equation (112) and the resulting Fig. 55 may still be used for the highest fields. It is reasonable to assume the truth of this, because the velocity of the ions in our picture never exceeds the velocity producing ionization for which Ohm's law was shown to hold. Furthermore, we were able to ascertain directly that the increase of the ratio I/E in strong fields is due to the increase of n and not of v . A very short time (about 0.01 sec.) after

the high field E had been applied for about 0.1 sec. to a thin sheet of glass, the current I' was measured at a low field E' in which the validity of Ohm's law is certain. The ratio I'/E' was found to be increased almost in the same way as I/E was observed to have increased, showing that it was the number of mobile ions that had increased.

A second difficulty arises in the heating produced by the current (*i.e.*, the increase of the number of ions may be partly due to the increase of temperature). We followed the increase of the temperature both by means of thermoelements and by the increase of the conductivity. It was found that heat equilibrium was reached under the conditions of our measurements after about 2 min. and that during the first second the change in the conductivity was negligible. We therefore used for our measurements of the current a time interval of 0.1 sec. The lapse of time between two measurements could then be reduced to 1 sec. In fact, on repeating the current measurements with the same potential many times in succession, we obtained the same values; thus the previous current did not affect the next one and the heat was not stored up by the process.

A third difficulty might arise from the sudden increase of the current to a very high magnitude producing instability in the circuit. This difficulty could be avoided by connecting in series with the dielectric an amplifying tube in which the saturation current was used. The magnitude of the current was thus limited by the heating current in the filament of the tube. We then measured the potential difference on the dielectric layer for a given current. We found that we were able to measure the dependence of the potential upon the current even when the current increased very rapidly with increasing field.

The current was measured, using the string electrometer and photographic registration on a moving film. A slowly rotating commutator increased the potential by equal steps of ΔV . Each potential was connected to one electrode during 0.1 sec. Between two charges both electrodes were connected for 1 sec. to earth.

If $\Delta V = 0$ and the applied potential V were the same, the current obtained was also the same. Below the ionization limit for fields of $10^4 - 5 \times 10^5$ volts per centimeter, the current was directly proportional to the potential

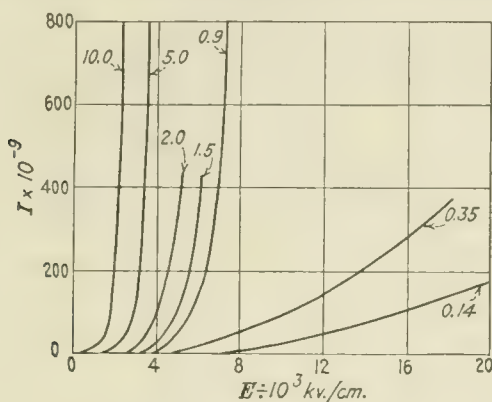


FIG. 58.

and the current increases in equal steps of ΔI according to Ohm's law. For fields in which the potential was such that the ionization limit was exceeded and ionization took place, the following relation between I and E was found

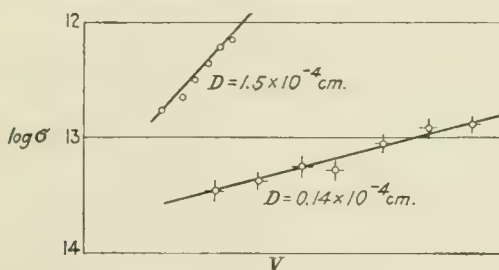


FIG. 59.

(Fig. 58) for glass sheets of different thicknesses lying between 0.14μ to 10μ .

These experiments explain an anomaly experimentally found by some investigators in high fields. Ohm's law seemed to fail and an expression of the form

$$\log I = aV + C, \quad (121)$$

was found to approximately represent the relation between the current and the applied potential. Comparing equation (121) with equation (109), we see that they are identical in a first approximation neglecting $\log \frac{V}{P}$ and taking $P = \text{constant}$. Figure 59 shows some data for two thin sheets of glass satisfying equation (121) fairly well. The current below the ionization limit could not be shown on the same scale. Figure 60 schematically represents the low field strength portion of the diagram on an enlarged scale, the vertical line corresponding to sheets thicker than $10\mu = 0.01$ mm.

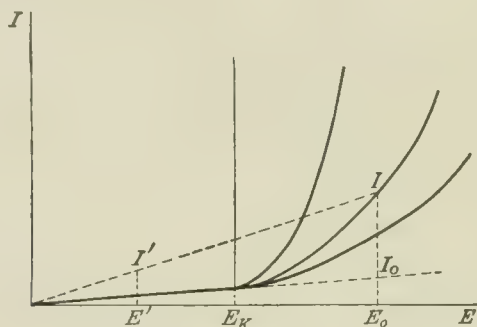


FIG. 60.

The shape of each curve ought to be represented by equation (108). However, as P is a function of E of the form given by equation (119) we cannot test equation (108) accurately. We may use it, however, in order to compute P and to test whether P will be the same on all curves for a given E . Plotting $\log I$ against E we find curves differing from a straight line. The slope of the curve is inversely proportional to P . We found that the slope increased with increasing fields E . It has, however, a definite value for each E . Plotting the value of P following from those curves as function of E we obtain the curve shown in Fig. 61.

Using equation (105) we found for glass: $n = 1$; $P_0 = 15$; $A = 2 \times 10^8$ volts/cm.,

$$P = 15 + \frac{2 \times 10^8}{E}. \quad (122)$$

In low fields P is about 200 volts while it diminishes to 15 volts in very strong fields. Thus the ionization potential for glass may be expected to lie between the limits 10 to 15 volts, a value not far different for that observed for molecules in gases. The number of ionizations for the same ion $z = V_c/P$ leading to a breakdown of the insulator is then about 15. The greatest distance d in which the ion accumulates energy at the field of $E = 5 \times 10^5$ volts per

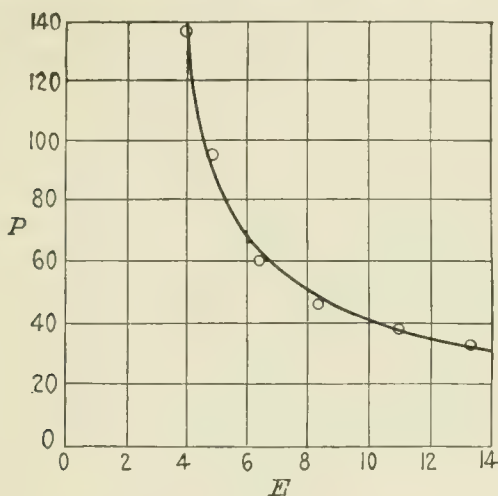


FIG. 61.

centimeter at which the first ionization begins may be as high as 5×10^{-4} cm. In the highest observed field $E = 1.5 \times 10^8$ volts per centimeter, the distance d is 10^{-7} cm., that is, a few atomic distances only. The mobility v , computed from equations (118) and (111), reaches in glass the surprisingly high value of about 1 cm./sec. per volt/cm., (if we assume the ion to be the Na^+ ion, $E = 3 \times 10^5$ to 5×10^5 volts per centimeter, $P_o = 10$ volts, the values should be 1.08 cm. per second per volt per centimeter and 1.8 cm. per second per volt per centimeter).

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LECTURE XVII

THE HIGHEST ELECTRIC FIELD

In dielectrics of a thickness less than 5μ the electric field may be raised above the ionization limit of 5×10^5 volts per centimeter to a breakdown field E_c where the number of collisions $E_c \cdot D/P$ reaches some critical value. Thus, in diminishing the thickness D , we increase the breakdown field E_c , as shown in Fig. 56.

It was found, however, that this rule holds up to a field of 1.5×10^8 volts per centimeter only, which is reached at a thickness of about 0.1μ . For thicknesses from 0.1μ down to 0.01μ the breakdown field remains constant, as shown on Fig. 57. Even a cooling to the temperature of liquid air did not increase this maximum value. It seems, therefore, that owing to some other mechanism a field of 1.5×10^8 volts per centimeter is the highest field which may be obtained in glass without a breakdown. Almost the same limit was found for mica.

The question then arises as to what the mechanism producing breakdown at a field 1.5×10^8 volts per centimeter, independent of thickness and temperature, is. It may be due to the electrodes, as, for instance, a mechanical rupture by the force attracting the electrodes, or to electrons pulled out from the metal into the dielectric. If it turns out that a mechanism *inside* the dielectric were responsible for the breakdown it would have to be different from the ionization by collision, since the influence of the thickness is the essential feature of a cumulative ionization, and this is absent in the ultimate breakdown.

Using different electrodes such as brass, mercury, lamp-black, water films, and ionized air, we found the limit of E_c always the same. Both in regard to a mechanical rupture and to a removal of electrons, the electrodes used are

so different in their action that those phenomena could not occur at the same field for all of them. For the same reason a heat conductivity at the surface is excluded. We conclude, therefore, that the cause must be looked for inside the dielectric. We notice that at the highest field the distance between two ionizing collisions reaches the order of magnitude of the atomic distance. It is, however, hard to see how this fact can be responsible for the inability of the dielectric to withstand higher fields. We should rather expect that as ionization occurs at first collision, the number of ionizations cannot be increased by an increase of the field, and hence this factor cannot act in this way. Thus, if the dielectric is able to support such a field without breakdown, it should also stand a higher field.

All considered, it seems most plausible to assume that the breakdown of glass in a field of 1.5×10^8 volts per centimeter is due to the ability of such a field to pull ions out of the glass. Apparently in this case we have to deal with an ionization by the field itself without a collision with another ion. This explanation seems likely when we consider that the force f exerted by this field on an ion,

$$f = Ee = 1.5 \times 10^8 \times \frac{1}{300} \times 4.77 \times 10^{-10} = 2.4 \times 10^{-4} \text{ dynes,}$$

is of the same order of magnitude as the force f' between two ions over an atomic distance of about 3×10^{-8} cm.,

$$f' = \frac{(4.77 \times 10^{-10})^2}{(3 \times 10^{-8})^2} = 2.5 \times 10^{-4} \text{ dynes.}$$

The assumption becomes even more plausible when we compare the work done by this field on an ion of the lattice. We may assume, for example, that the ion is held by elastic forces such that it is able to vibrate with a frequency corresponding to the residual rays of $\lambda = 40\mu$ in wave length. The elastic energy of an ion displaced by a field E will be given by

$$W = \frac{E^2 e^2 \lambda^2}{8\pi^2 c^2 m}$$

For a sodium ion we obtain from this relation the value $W = 3.3 \times 10^{-13}$ ergs, which is decidedly higher than the average energy of heat agitation at room temperature, i.e., $W_t = 7 \times 10^{-14}$ ergs. It is only at 1600° abs. that the average heat energy becomes equal to this energy, and at this temperature the crystal has already melted. That is, such fields are able to do work on a crystal greater than that required to melt it.

	Highest field 1.5×10^8 volts per centimeter	Usual field 3×10^5 volts per centimeter
1 Force exerted on an ion $f = E \times e$	2.4×10^{-4} dynes	4.8×10^{-7} dynes
2 Attraction of the electrodes $p = \frac{\epsilon E^2}{8\pi}$; $\epsilon = 6$	6×10^{10} dynes per cm. ² $= 6 \times 10^4$ Atm.	2.4×10^5 dynes per cm. ² $= 0.24$ Atm.
3 Specific energy per cm. ³ of the field $u = \frac{\epsilon E^2}{8\pi}$	6×10^{10} ergs per cm. ³ $= 1.4 \times 10^3$ cal. per cm. ³	2.4×10^5 ergs per cm. ³ $= 5.6 \times 10^{-3}$ cal. per cm. ³
4 Energy of an ion displaced by the field $W = \frac{E^2 e^2 \lambda^2}{8\pi^2 c^2 m}$; $\lambda = 40\mu$	3.3×10^{-13} ergs, or 0.2 volts	1.3×10^{-18} ergs, or 8×10^{-7} volts
Kinetic energy of a gaseous atom reaches the same value at a temperature $T = \frac{2}{3K}(W)$	1600° abs.	0.006° abs.
5 Potential difference which exists in the field between two ions of the same sign over a distance $2a = 5.0 \times 10^{-8}$ cm. $V = E \times 2a$	7.5 volts	0.015 volts
6 Tension between the lattice of positive ions and the interposed lattice of negative ions separated by $2a$ in the field $J = \frac{Ec}{4a^2}$	10^{11} dynes per cm. ² $= 10^5$ Atm.	2×10^3 dynes per cm. ² $= 200$ Atm.
7. Number of ions per cm. ² bound on the elec- trode by the field. $n = \frac{\epsilon E}{4\pi e}$ (The number of ions in one atomic layer $n_0 =$ 4×10^{14} assuming $2a = 5 \times 10^{-8}$ cm.)	5×10^{14} charges per cm. ²	10^{12} charges per cm. ²

In order to further describe the possible effects of the highest fields of 1.5×10^8 volts per centimeter, we may compare some data computed for this field with the corresponding data for the field 3×10^5 volts per centimeter, which is about the breakdown field for thick sheets and causing cumulative ionization by collision.

The data of the table on p. 177 show unquestionably that with such fields as are observed in thin plates, we attain fields that equal those predicted from our theory of crystal structure as outlined in Lecture XV. Furthermore, we see that not only the field itself is exceptionally high, but it exerts mechanical actions exceeding any pressure obtainable by a compressor and even exceeds the internal pressures of liquids. The energy concentration is remarkably high—of the same order of magnitude as in chemical reactions. The strong fields obviously furnish a new means of producing electrical effects of a magnitude exceeding any ever used before. A new field of investigations seems to be opened by the possibility of exerting forces of the same order of magnitude as the chemical and molecular forces. One might enumerate some of the experiments which are now in progress and seem to furnish valuable results, as well as others that seem possible.

1. The high compression produced in the dielectric by the attraction of the electrodes may be used for measuring the compressibility. We saw that Hooke's law must be regarded as the first approximation only. At sufficiently high *tensions* the *attracting* forces must become predominant. Furthermore a *high compression* furnishes us the best means of determining the law of the *repelling* forces. The latter forces are the least known and therefore their investigation is one of the most important problems of the electrical theory of crystal lattices. The pressure exerted by the electrodes is easily computed for a uniform field E . If the field is not uniform due to space charges the attraction of both electrodes must be different and the pressure inside the dielectric will not be uniform. The

attraction of both electrodes must therefore be separately measured.

The strain produced in the dielectric is best measured by means of *X*-rays in a crystalline plate, using soft monochromatic rays and an electrode consisting of a water film or of gas ions. A displacement of the spectral line while the dielectric was subjected to the electric field has been actually observed. It is especially desirable in such work to use crystals of the molecular type.

2. Closely connected to the deviation from Hooke's law is the change of the frequencies of the ions in the crystal manifested by the residual rays. Zwicky computed the effect which is to be expected and found that it is still more pronounced than the change in the bulk modulus.

3. The deviation from Hooke's law for the ions of the crystal lattice must be manifested by an increase of the part of the dielectric constant, due to a displacement of the ions.

In liquids with polar molecules a field of 10^8 volts per centimeter is presumably sufficient to produce an orientation of the greater portion of the molecules. In fact, assuming an electric moment of 2×10^{-18} , corresponding to two opposite elementary charges 0.4×10^{-8} cm. apart, we find for this molecule in an electric field of 1.5×10^8 volts per centimeter an orientation energy of 10^{-12} ergs, while the energy of heat movement at room temperature is about twenty times less— 6×10^{-14} ergs. Therefore the part of the dielectric constant due to the orientation of molecules must vanish and the dielectric constant will drop from a high value of 20 to 80 down to 3 to 4, which is the square of the refractive index.

4. Another effect of a displacement of ions produced by the high electric fields should be noticeable in the intensity of reflections of *X*-rays from different crystallographic planes. The most striking example may be found on KCl crystals in the direction (111). Those planes are alternately composed of potassium and chlorine ions, which have the same number of electrons, 18. For *X*-rays both

systems of planes are therefore equal and the lattice acts as a grating with a distance equal to that between K^+ and Cl^- . The displacement of ions in opposite directions must destroy this regularity. The distance in the direction of the field must be considerably larger between Cl^- and K^+ than between K^+ and the next Cl^- . The only periodicity in the lattice would then correspond to the distance between K^+ and the next K^+ or between two successive Cl^- ions. The reflection corresponding to the distance from K^+ to Cl^- must then become fainter and finally disappear. It will do this first in reflections of a higher and then in those of a lower order.

5. The orientation of polar molecules in liquids may also be observed by means of X-ray photographs, which must change from circles to lemniscates and ellipses. The orientation of molecules on the surface must be followed by a change in the contact potential of the dielectric, and by a change in the chemical behavior.

6. A direct indication of the effect of orientation would be given by the effects of double refraction both in crystals and liquids, as manifested by the Kerr effect.

7. The attraction of a liquid electrode to the dielectric exceeds the surface tension many times. It was to be expected, and was actually observed in the use of mercury, that the angle of contact with the surface of the dielectric changed with high fields. At high fields mercury adheres to glass just as well as alcohol does. The influence of the field on the surface tension is a convenient means for measuring quantitatively the attraction of the electrode and thus actually measuring the field at the surface, which may be different from the average field defined by the ratio of the potential difference to the distance between the electrodes. In the event that the attraction is much stronger at one electrode than at the opposite one, we may conclude that the ions of the same sign as the strongly attracted electrode are mobile.

8. The field must change the surface pressure and consequently the heat of vaporization and the vapor pressure

of the saturated vapor over a liquid electrode. The attraction is primarily exerted on the ions. The number of ions of one sign which must be stored up on the surface in order to compensate the field is 5×10^{14} per cm^2 . This corresponds to the number of ions of one sign which may be stored up at the surface of metals, so that the fields may not be manifested externally. This is highly improbable, however, in the case of a liquid like water as there are not enough mobile ions. Thus the field must penetrate to a depth measured by some hundred atomic layers at least. Sheets of such thickness are visible. Accordingly, it is not surprising that we observed that a water film used as an electrode could not be evaporated in 2 hours even at 80°C ., while the surface which was not charged became absolutely dry. The vapor pressure is being investigated as a function of the electric field and of the thickness of the water film.

9. No influence was found upon the electrical resistance of the thin metallic layers used as electrodes in such fields, contrary to some observations reported in the literature on this subject. In spite of the fact that the field used by Anton Walther was 34×10^6 volts per cm ., instead of 3×10^4 volts per cm ., the resistance of even very thin transparent sheets of platinum and nickel remained constant within less than 0.1 per cent.

10. A very interesting effect was found by Miss Arsenjewa corresponding to the Stark effect on gas molecules in an electric field. At low temperatures, when the heat movement vanishes, the regularity of a crystal lattice is as complete as the equality of molecules in a gas. The absorption and reflection spectrum consists of very sharp lines, corresponding to some energy levels of electrons in the crystal. A displacement and splitting of those lines must be expected in the field which is about one thousand times the highest field used in gases. Miss Arsenjewa was actually able to find a spreading of the absorption and reflection lines on crystals of ruby at liquid-air temperatures in the high fields.

It is obvious that many more problems might be added, especially a great variety of physical chemical problems.

The strong electric fields which may now be obtained without breakdown of dielectrics also have important technical applications.

1. It should be possible to construct insulators in such a way as to prevent a cumulative ionization through the whole dielectric. The potentials which such dielectrics will then stand will be much higher than for the usual insulators of the same thickness.

2. If such thin sheets of insulators can be constructed, condensers of a very high capacity and of a high breakdown potential may be manufactured.

3. Such condensers can be used as storage batteries, giving a high degree of concentration of energy.

4. The attractive forces mentioned above could be used to replace electromagnets, relays, etc.

5. The compression of the dielectric can be used for all kinds of a transfer of electric energy into elastic energy, especially in the production and transfer of sound waves and rapidly alternating pressures.

6. The ionization by collision by such fields might be used as an effective amplifying device.

In the first place, a more detailed investigation of the mechanism of the ionization is needed. The manner in which the puncture occurs after the ionization produces the necessary number of ions must be discovered. More substances must be investigated and the fundamental constants of the present theory determined. The heat conductivity at different temperatures up to the melting point must be known in order properly to calculate the breakdown by heat. The field E_c , at which ionization by collision begins, the ionization potential P_c , the dependence of P upon E , the accurate conditions of a breakdown, and the potential distribution after ionization begins must be found for the most important types of dielectrics in order to apply the theory of breakdown by ionization.

The maximum field required to pull out ions from the dielectric must be measured and the maximum dielectric strength must be measured for the principal types of dielectrics, so that its calculation on the basis of the electrical theory of crystal lattices can be achieved.

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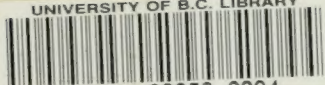
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